Relativistic Effects and the Chemistry of Gold*

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In atoms of high nuclear charge (Z), as a consequence of a relativistic effect, the s electrons of an atom become more bound and their orbitals smaller than if this effect were absent. Simultaneously, the d (and f) electrons are less bound because of this effect, which scales roughly as Z^2. Gold exhibits a large relativistic effect. This accounts for gold being more resistant to oxidation than silver. It also accounts for higher oxidation states being more accessible in gold than in silver. These effects are illustrated by some fluorine chemistry of gold and silver.

Differences in the chemistry of gold compared with that of silver, particularly the initial resistance of gold to oxidation, and its greater extent of oxidation once oxidized, can be attributed largely to the impact of a relativistic effect. The importance of this for gold chemistry was noted by Pitzer (1) and Pyykkö and Desclaux (2) nearly twenty years ago. More recently Kaltsoyannis (3) has summarized the impact of the effect for inorganic and organometallic chemistry.

As atomic nuclear charge (Z) increases, electrons that penetrate to the nucleus (the **s** electrons) increase their average velocity and as a consequence of relativity, their mass. This relativistic effect causes the **s** electrons (and to a lesser extent, the **p** electrons) to be in smaller orbitals than if this effect were absent. Therefore, in the heavier elements, the **s** electrons are more strongly bound and shield the nuclear charge from the other electrons (especially **d** and **f**) more effectively than if the relativistic effects were absent. The **d** and **f** electrons are therefore less bound and occupy larger orbitals when relativistic effects are large. These effects scale roughly with Z^2 and become important for elements heavier than the lanthanides (4). For the elements gold to bismuth the impact on energies is comparable with chemical bond energies (1). Indeed, gold, because it is also at the end of the **5d** orbital filling, (third transition series contraction effect) following on the **4f** filling (lanthanide contraction) exhibits maximum impact of this relativistic effect (2-4).

As a consequence of the lanthanide contraction and the relativistic effect we expect that the effective size of the isolated gold (gaseous) atom will be comparable with that of silver, although presently neither atom size is known. What is known, however, is that the relativistic effect in gold enhances the binding of the **s** electrons relative to those of silver. This accounts for the smaller size established by Schmidbaur and his coworkers [5] for Au(I) versus Ag(1); the high electron affinity of gold relative to silver (see Table 1), and for the existence of the aurides (*eg* Cs^+Au^-) which are non-metallic semiconductors (6). It is also why the first ionization potential of gold (removing the **s** electron from the **5d¹⁰6s** configuration) is so much higher than that of silver (see Table). The tighter binding of the **s** electrons of gold also accounts for the greater cohesion energy of gold metal since the valence **s** electron contributes most to that bonding. The enthalpies of atomization (see Table) reflect this. The tighter binding of the valence **s** electron of gold also contributes to the higher melting point, and smaller atom to atom close contact in the metal. The raising of the Au **5d** electron energies and the lowering of the valence **6s** also accounts for the yellow color of gold (absorption beginning at ~2.38eV) associated with transitions from the **5d** band to the Fermi level (largely **6s** in character) (11).

Table 1 *Comparing Gold with Silver*

			Au		Ag		Refs
Ionization potentials (eV)	1st: 2nd:		9.225 20.5		7.576 21.49	}	7
Electron affinity (eV)			2.039		1.202		8
Heats of atomization (kjoules mol^{-1}) Melting point (°C)			368 1063		285 961	}	9
A-A distance in f.c.c. cells (Å), 25°C :			2.8840		2.8894		10

The related absorption in silver (**4d** band to the Fermi level of ~**5s** character) is in the ultraviolet, at ~3.7eV.

Detailed appraisals of the impact of the relativistic effect upon the size of Au(I) versus Ag(I) have already been given by Schmidbaur and his coworkers (5) and have been summarized in this journal (12). In this paper, emphasis is given to the impact of the effect on the attainment of higher oxidation states in gold, compared with silver.

As we have seen, the consequences of the relativistic effect have prime impact in causing metallic gold to be more resistant to oxidation than silver. If a sufficiently potent oxidizer is available however, gold can be oxidized to a higher oxidation state than silver, and again this is a consequence of the relativistic effect. Fluorine usually excites the highest and the greatest range of oxidation states for an element. This is so for gold and silver. It is in the fluorine chemistry of these elements therefore that the large relativistic effect in the chemistry of gold is best seen.

SOME FLUORINE CHEMISTRY OF GOLD AND SILVER

Chemistry in liquid anhydrous hydrogen fluoride

When metallic gold is exposed to elemental fluorine (F_2) at room temperature in the presence of the ionizing solvent liquid anhydrous hydrogen fluoride (aHF) containing an alkali fluoride, the metal is quickly dissolved to give the alkali salt of the anion AuF_4^- (13):

$$Au_{(s)} + F^-_{(solv)} + \tfrac{3}{2}F_{2(g)} \xrightarrow{\text{aHF}_4, \sim 20°C} AuF_4^-{}_{(solv)} \quad (1)$$

Under similar conditions silver is oxidized only to the +2 oxidation state, the ultimate product being AgF_2, which is not soluble in aHF. If however the F_2 is photo- dissociated to atoms (sunlight will do) the AgF_2 is further oxidized and dissolves in the aHF made basic with alkali fluoride (14):
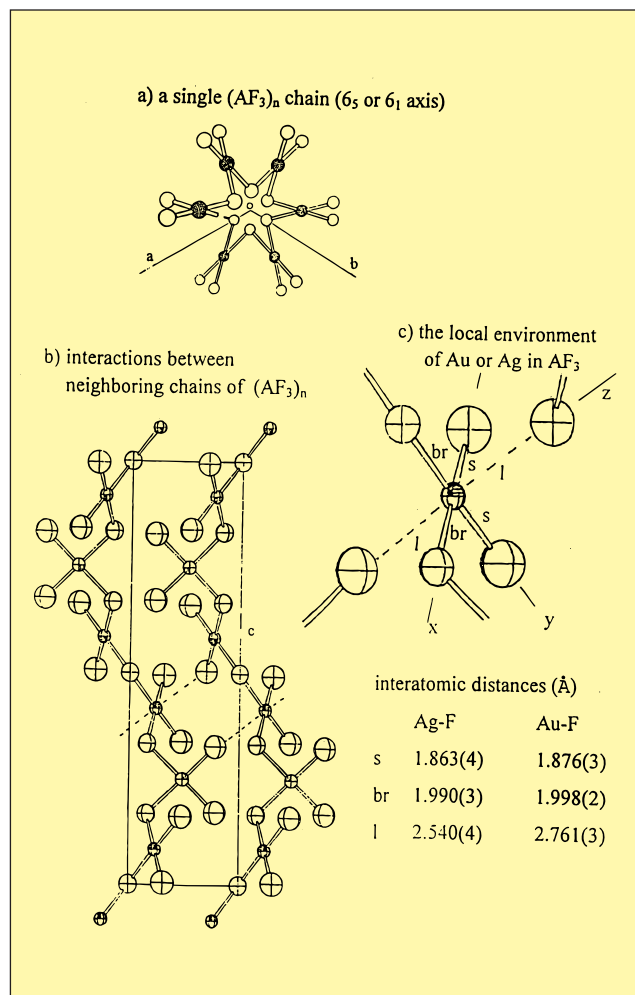
$$AgF_{2(s)} + F^-_{(solv)} + F^\bullet_{(solv)} \xrightarrow{\text{aHF}, \sim 20°C} AgF_4^-{}_{(solv)} \quad (2)$$
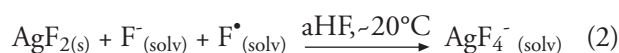
Under such conditions (of photo-dissociated F_2) AuF_4^- is oxidized further, to AuF_6^- (15):

$$AuF_4^-{}_{(solv)} + 2F^\bullet_{(solv)} \xrightarrow{\text{aHF}, \sim 20°C} AuF_6^-{}_{(solv)} \quad (3)$$
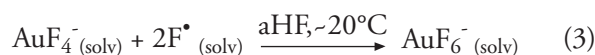
These reactions clearly demonstrate how much more easily the **5d** electrons of gold can be involved in bonding than can the **4d** electrons of silver. The stronger binding of the silver **4d** electrons is already indicated (see Table) by the second ionization potential, which is about 1eV higher than that of Au. Not only are the Au **5d** electrons less firmly bound than the Ag **4d**, but **5d** orbitals are also much larger than the **4d** of Ag. This is clearly shown by related Au(III) and Ag(III) structures.

Comparison of the structures of Au(III) and Ag(III)

The structures (16) of AuF_3 and AgF_3 are represented in Figure 1. In the approximately square arrangement of four F ligands about each A (A = Au or Ag) atom (in the local xy plane) the Au-F interatomic distances are slightly larger than those of Ag-F, but not significantly so. Simpler comparison of square coordinate A(III) is made, in $[AF_4]^-$ salts, where all four A-F distances are equivalent. For $KAgF_4$ (17), Ag-F= 1.899(3)Å and for $RbAuF_4$ (18), Au-F = 1.915(3)Å. The bonding in the square coordinate AF_4^- (and related units in AF_3) uses four A oribitals and four ligand orbitals. The A orbitals are the valence **s**, two **p** orbitals, and a **d** orbital. As we have seen, the valence **s** orbital of Au should provide better binding energy than that of silver, but this is largely offset by the poorer binding provided by the **5d** orbital of Au compared with the **4d** of Ag. The impact of the relativistic effect on **p** orbitals is complex (1, 2, 4) and in such cases as $[AF_4]^-$ is probably slight. The overall relativistic impact on the binding in square-

a) a single $(AF_3)_n$ chain (6_5 or 6_1 axis)

b) interactions between neighboring chains of $(AF_3)_n$

c) the local environment of Au or Ag in AF_3

interatomic distances (Å)

	Ag-F	Au-F
s	1.863(4)	1.876(3)
br	1.990(3)	1.998(2)
l	2.540(4)	2.761(3)

Figure 1 *Comparison of the fluorine ligand arrangement about the gold and silver atoms in the structurally related trifluorides AuF_3 and AgF_3 (reference 16)*

coordinate A(III) is therefore small. The big difference, however, in both the AF_3 and $[AF_4]^-$ salt structures, lies in the size of the 'non-bonding' valence **d** orbitals of the A(III).

As may be seen from the Figure, the interatomic distances of AF_3, approximately normal to the close-bonded AF_4 groups, are long in each case, but the Au..F distance is 0.22Å longer than Ag…F. This can be attributed to the larger size of the gold 'non-bonding' valence **d** electron pair that occupies the local z-axis region. This greater size of the 'non-bonding' valence **d** electron orbitals of gold, relative to those of silver, is of course consistent with the weaker binding of Au **5d** electrons versus the Ag **4d**. It is also revealed in the formula unit volumes of the AF_3 and the $[AF_4]^-$ salts. Each gold compound is ~5Å^3 larger, per formula unit, than its silver counterpart. This is in harmony with the observed chemistry.

Contrasting the instability of AuF_2 with the stability of AgF_2

The relativistic effect also accounts for the observed instability (19) of AuF_2 with respect to metallic gold and Au(III) products. Although the large and highly stable anion SbF_6^- does provide (19) for the preparation of the simple-paramagnet $Au^{2+}[SbF_6]_2^-$, the interaction of this with excess alkali fluoride in aHF leads to complete disproportionation of the Au(II):

$$8F^-_{(solv)} + 3Au^{2+}_{(solv)} \xrightarrow{\text{aHF, ~-20°C}} Au_{(s)} + 2AuF_4^-{}_{(solv)}$$
(4)
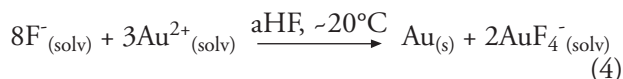
Similar treatment of $Ag^{2+}[SbF_6]_2^-$ gives AgF_2 and the alkali salt of SbF_6^-. This facile disproportionation of Au(II) to Au(0) and Au(III) and the absence of such disproportionation for Ag(II), expresses the tighter binding in A(0) provided by the **6s** electron of Au, and the easier engagement of the **5d** electrons of Au (compared with the **4d** of Ag) in the formation of A(III).

Concerning AuF_6^-, AgF_6^- and the possibility of preparing AuF_6

As the ready oxidation of AuF_4^- to AuF_6^- {equations (3)} illustrates, the 'non-bonding' z axis **d** orbital electron-pair of the Au(III) is easily engaged in bonding by two F atoms, which add. In contrast AgF_6^- solution species have not been similarly preparable from AgF_4^-, even using the most potent of known oxidative fluorinators, KrF_2 (20).

As we have seen it is relatively easy, with fluorine, to obtain Au(V) but can higher oxidation states than this also be realized? Of particular interest is the molecule AuF_6. The hexafluorides of the third transition series are known from tungsten through to platinum and the electron affinity of each of these gaseous molecules is greater by ~1eV for each unit increase in atomic number of the metal (21). The electron affinity of PtF_6 is nearly 8eV, and $E(AuF_6)$ is expected (22) to be 1eV higher. Miyoshi and Sakai (23) have calculated $E(AuF_6)$ to be 9.56eV, in agreement with that rough estimate. This means, of course, that the AuF_6^- is difficult to oxidize. Cationic Ag(III) and Ni(IV), which are potent oxidizers in liquid HF, are able to oxidize PtF_6^- to PtF_6 but not AuF_6^- to AuF_6 (24). It is possible that the remaining valence **d** orbital electrons of gold in AuF_6^- (which constitute a ligand-field stabilized t_{2g}^6set) are too tightly bound for chemical electron-oxidation, but if so the possibility of electrochemical generation of AuF_6 still remains available. Higher oxidation states than Au(VI) appear to be beyond access.

CONCLUSIONS

In comparison with silver, the greater resistance of gold to oxidation, and the greater range of its oxidative chemistry, have been related to a relativistic effect. This causes the gold **s** electrons to be more bound, and the **d** electrons to be less bound, than their counterparts in silver. Although, for the closely bound set of F ligands (in square array) in A(III) fluorospecies (A=Au, Ag) the Au(III) has nearly the same effective size as Ag(III), this is not the case for the non-bonding valence **d** orbital electrons. The Au(III) **d** electron-pair, normal to the $[AuF_4]$ short-bonded set in AuF_3, gives the Au(III) ~0.22Å greater effective radius than its silver relative, in that direction. This correlates with the weaker binding of the Au **5d** electrons and with the facile addition of two F atoms to AuF_4^- to yield AuF_6^-.

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The author is an emeritus professor of chemistry and a principal investigator in the Division of Chemical Sciences, Lawrence Berkeley National Laboratory. His research interests have largely been concerned with the highest attainable oxidation states of the noble metals, and noble-gas chemistry.

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