

4 Silver and gold

4.1 Introduction

For many years, the chemistry of silver and gold was believed to be more similar than is now known to be the case [1–10]. In the Cu–Ag–Au triad, the stability of oxidation states does not follow the usual trend of increasingly stable high oxidation state on descending the group; for copper, the +2 state is the most important, for silver it is the +1 state and, though oxidation states between –1 and +7 are claimed, for gold it is the +1 and +3 states that dominate its chemistry. The types of compound are summarized in Table 4.1.

A plausible reason (or one of the reasons) for the relative stabilities of the oxidation states lies in the ionization energies (Table 4.2) [11]. The value of I_1 is lower for silver than for copper, as would be expected, but I_2 is higher for silver (this electron is removed from a 4d orbital, where the electrons are farther apart and repelled less, than in 3d orbitals); I_3 is again lower for silver, correlating with the increased stability of silver(III) and the tendency of silver(II) to disproportionate. The high I_1 value for gold results from the relativistic contraction of the 6s shell (from which this electron is removed) while the low I_3 value is in keeping with the stability of the +3 state, reinforced by the large ligand field splitting for the $5d^8$ ion. The preference of gold for the +3 state has been attributed to relativistic effects, according to Hartree–Fock calculations [12].

All three M^+ ions are known to form compounds with the unusual digonal linear coordination (see also section 4.9.7), though this is most common for gold. As a result, complexes R_3PMX of copper and silver are normally di- and tetranuclear species with 3- or 4-coordinate metals, while the gold analogues are 2-coordinate monomers. This is the reverse of what would be expected on steric grounds [13, 14].

Mixing of gold $5d_{z^2}$ and 6s orbitals, facilitated by the small d^{10} – d^9 s separation (and also the large d^9 s– d^9 p separation, Table 4.3) gives rise to two orbitals Ψ_1 and Ψ_2 (Figure 4.1). The electron pair initially in $5d_{z^2}$ occupies Ψ_1 , away from the two ligands (considered to lie along the z axis). The orbital Ψ_2 can mix further with $6p_z$, to afford two orbitals Ψ_3 and Ψ_4 , which have (empty) lobes pointing along the z axis that can accept electron pairs from the two ligands (Figure 4.1). Recent Hartree–Fock calculations do indicate significant 5d involvement.

Table 4.1 Compounds of copper, silver and gold

Oxidation state	Copper	Silver	Gold
-1			With very electropositive metal (e.g. Cs ⁺ Au ⁻)
+1	Stable if insoluble or complexed; usually 4-coordinate	Found with variety of ligands, e.g. NH ₃ , PR ₃ , Cl; usually 4-coordinate	Occurs with wide range of ligands; most often 2-coordinate
+2	Stable in aq. solution; found with wide variety of ligands, 4-6-coordinate	Usually found with N-, O-, F-donors; 4-6-coordinate	Rare, stabilized by 'suspect' ligands
+3	Rare, usually stabilized by F	Most often found bound to N, O, F; 4- and 6-coordinate	Common with wide range of ligands; usually square planar
+4			One example with a 'suspect' ligand
+5			Fluorine as ligand 6-coordinate
+7			Not confirmed, F as ligand

4.2 The elements and uses

Both silver (m.p. 962°C, b.p. 2212°C) and gold (m.p. 1065°C, b.p. 2807°C) have characteristic brilliant white and yellow colours in bulk but when finely divided are black or, in the case of gold, can be purple, ruby red or blue. Thus reduction of gold compounds by SnCl₂ gives the colloid known as 'Purple of Cassius', which is used as a ceramic colorant.

Table 4.2 Ionization energies (kJ mol⁻¹)

	Cu	Ag	Au
<i>I</i> ₁	745	731	890
<i>I</i> ₂	1958	2073	1978
<i>I</i> ₃	3554	3361	(2900)
<i>I</i> ₄	5326	(5000)	(4200)

Estimated values in parentheses.

Table 4.3 Energy separations (eV)

	Cu ⁺	Ag ⁺	Au ⁺
d ¹⁰ -d ⁹ s	2.72	4.86	1.86
d ⁹ s-d ⁹ p	5.72	5.07	5.96
d ¹⁰ -d ⁹ p	8.44	9.93	7.82

Neither metal is attacked by oxygen, but silver reacts with H_2S in town air forming a black tarnish of Ag_2S . Both dissolve in cyanide under oxidizing conditions. Non-oxidizing acids have no effect, but silver dissolves in concentrated HNO_3 and gold in aqua regia. Both silver and gold react with the halogens, and gold can, therefore, be dissolved in mixtures of halogens and ionic halides in a polar solvent (e.g. $\text{Cl}_2/\text{Et}_4\text{NCl}/\text{MeCN}$ or $\text{I}_2/\text{KI}/\text{MeOH}$) [15].

Like copper, both gold and silver have fcc (ccp) lattices ($\text{Au}-\text{Au}$ 2.88 Å, $\text{Ag}-\text{Ag}$ 2.889 Å) in which the metals are 12-coordinate.

4.2.1 Extraction [16]

Although silver does not often occur native, principal ores are AgCl ('horn silver') and Ag_2S (argentite), sometimes associated with copper ores; main ore-containing countries are Mexico, Canada, Peru, Australia, the USA, the former USSR and Poland. Gold is largely formed as the metal (USA, former USSR, South Africa, Canada) deposited in quartz, though erosion can lead to veins in rocks or deposits in rivers; it is sometimes found in sulphide minerals like pyrites and chalcopyrite (CuFeS_2) or arsenopyrite (FeAsS). Bacteria have been implicated in the accumulation of gold while various complexes like AuCl_2^- and $\text{Au}(\text{SH})_2^-$ are thought to also be responsible for gold transport and accumulation.

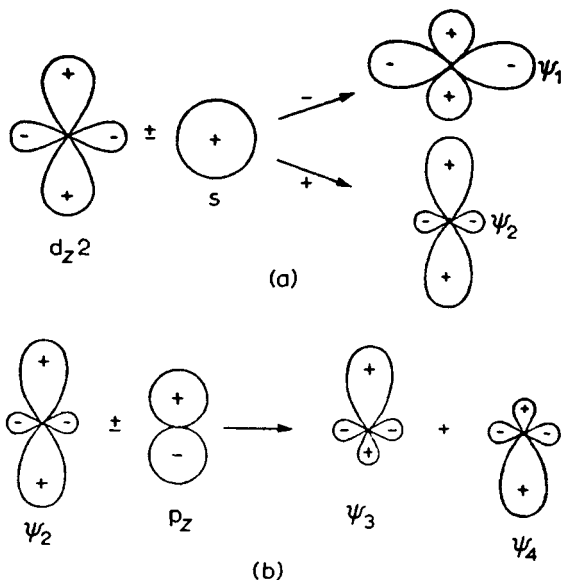


Figure 4.1 Mixing of atomic orbitals to give hybrid orbitals capable of generating digonal 2-coordination. (From J.E. Huheey, *Inorganic Chemistry*, Harper and Row, London, 1975. Reprinted by permission of Addison-Wesley Educational Publishers Inc.)

Silver was formerly extracted by cyanide solution of Ag_2S , the resulting $\text{Ag}(\text{CN})_2^-$ being treated with zinc to afford the metal; roasted ores could also be extracted with mercury to give silver amalgam. Presently much silver is extracted by workup of the anode slime from the preparation of non-ferrous metals (Pb, Cu); pure silver is obtained by electrolysis of AgNO_3 .

Gold ores can be concentrated by froth flotation, the resulting concentrate being roasted at $600\text{--}800^\circ\text{C}$ to oxidize off sulphur and arsenic as their oxides. The product is extracted with cyanide under oxidizing conditions (using either peroxide or air itself) before displacement with powdered zinc. More reactive metals (silver etc.) can be removed by chlorination of molten gold.

An alternative route increasingly investigated is bio-oxidation using bacteria to oxidize pyrite or arsenopyrites at 45°C .

Final purification can be done by electrolysis using HAuCl_4 electrolyte.

4.2.2 Gold plating and other methods of gold deposition

Electrolysis of solutions containing $\text{Au}(\text{CN})_2^-$ is widely used to recover gold from solution (electrowinning) [17]. The process is also used to deposit gold coverings for electrons (e.g. printed circuit boards, electrical connectors) and most recently for hip and shoulder joint replacement surgery.

Where insulated surfaces are to be joined, two other processes are employed: the 'immersion' and 'electroless' methods. Immersion gold plating is based on displacement reactions, where a copper or nickel object is coated with a thin film of gold from a solution of gold complex, usually in slightly acid solution (about 90°C); the process is self-terminating when a film of *c.* $0.2\ \mu\text{m}$ is attained. Electroless processes use a reducing agent (NaBH_4 , dimethylaminoborane, sodium hypophosphite) usually in hot alkaline solution ($70\text{--}90^\circ\text{C}$) to reduce a gold complex such as $\text{Au}(\text{CN})_2^-$.

4.3 Halides

The halides of silver and gold are listed in Table 4.4; as expected gold has more in higher oxidation states [18c].

4.3.1 Silver halides

The subfluoride Ag_2F can be prepared by reaction of silver with aqueous AgF or by electrolysis of AgF in HF :



It has the anti- CdI_2 structure, with alternating double layers of silver and intercalated fluorides. It is a metallic conductor.

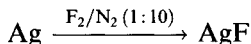
Table 4.4 Characteristics of silver and gold halides

	Silver				Gold			
	F	Cl	Br	I	F	Cl	Br	I
M_2X	Bronze							
MX	Colourless, m.p. 435°C	Colourless, m.p. 455°C	Cream, m.p. 432°C	Yellow, m.p. 558°C		Yellow-white, dec. 170°C	Light yellow, dec. 115°C	Lemon, dec. 120°C
MX_2	Black					Black ^a		
MX_3	Bright red ^b				Gold-yellow, dec. 500°C ^b	Red, dec. 254°C	Dark brown, dec. 97°C	
MX_5					Yellow-brown			
MX_7					Pale yellow			

M, silver or gold; X, halide.

^a $AuCl_2$ is, in fact, Au_4Cl_8 , containing Au(I) and (III); ^b Ag_3F_8 and Au_2F_5 are also obtained.

Anhydrous AgF is best made by fluorination of finely divided silver at room temperature; alternatively it can be made by dissolving silver(II) oxide in hydrofluoric acid and crystallizing:



As expected from the similarity of ionic radii between Ag^+ (1.15 Å) and Na^+ (1.01 Å), one form has the NaCl structure (it is trimorphic) with other forms having the CsCl and inverse NiAs structures. Unlike the other silver(I) halides, it is very soluble in water (up to 14 M) and forms di- and tetrahydrates; it is decomposed by UV rather than visible light and melts unchanged at 435°C.

The other silver(I) halides are traditionally prepared by ionic precipitation, on account of their insolubility:



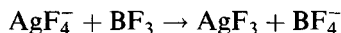
which increases in the order $\text{Cl} < \text{Br} < \text{I}$, just as their covalent character increases and their colour deepens (as the energy of the charge transfer process $\text{Ag}^+\text{X}^- \rightarrow \text{AgX}$ decreases) [19]. AgCl and AgBr also have the 6-coordinate NaCl structure but the repulsion between I^- in a NaCl-type lattice is such that the stable (γ) form at room temperature of AgI has the 4-coordinate ZnS structure. Comparison between experimental lattice energies (derived from Born–Haber cycle calculations) and values calculated using the Kaputinskii equation show increasing discrepancy in the order $\text{F} < \text{Cl} < \text{Br} < \text{I}$, demonstrating increasing divergence from an ionic model as the larger halide ion becomes more polarizable by Ag^+ (this contributes to the lattice energy being greater than predicted on an ionic model, which in turn leads to a more positive enthalpy of solution, sufficient to ensure their insolubility rather than the solubility predicted from the similarity in size between Ag^+ and Na^+). Silver iodide also exists with the hexagonal ZnO structure (136–146°C); above 146°C, it passes into the α -form which has a rigid bcc structure in which there is a fixed array of I^- , but the Ag^+ can move almost at will through the structure. This causes α -AgI to have the highest conductivity of any ionic solid: interest has centred on creating ionic conductors with high conductivities at room temperature [20].

The silver(I) halides are, of course, important in the photographic process, AgBr being most commonly used; in this process a photon causes an electron to be lost from a halide ion and gained by a silver ion, thus forming silver atoms. Subsequent development with hydroquinone intensifies the image by reducing those AgBr grains containing silver atoms, followed by ‘fixing’ the image, a process in which thiosulphate removes unreacted AgBr as the complex ion $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$. Since the light-sensitive AgBr has been removed, the image is now stable.

Silver(II) fluoride AgF_2 is a genuine silver(II) compound exhibiting Jahn–Teller tetragonal distortion (4F at 2.07 Å; 2F at 2.59 Å); it exhibits a low

magnetic moment ($1.07 \mu_B$) owing to anti-ferromagnetic coupling. In the absence of excess fluorine, it decomposes at $150\text{--}200^\circ\text{C}$ but under a fluorine atmosphere melts at $\sim 620^\circ\text{C}$. It is prepared from the elements at 200°C and is quite a strong fluorinating agent.

AgF_3 has recently been characterized [21] as a red diamagnetic solid, isostructural with AuF_3 ; it is best made by adding a fluoroacid (BF_3 , PF_5) to solutions of AgF_4^- salts in anhydrous HF



The elongated octahedral coordination of silver has $\text{Ag}\text{--}\text{F}$ 1.863 \AA ($\times 2$) 1.990 \AA ($\times 2$) and 2.540 \AA ($\times 2$). When dry, it is stable for some weeks at room temperature, though it loses fluorine on standing in HF to form Ag_3F_8 and is a strong fluorinating agent. Ag_3F_8 is $\text{Ag}^{\text{II}}\text{Ag}_2^{\text{III}}\text{F}_8$ ($\mu_{\text{eff}} = 1.92 \mu_B$); Ag_2F_5 ($\text{Ag}^{\text{II}}\text{Ag}^{\text{III}}\text{F}_5$) has also been made.

4.3.2 Gold halides

Only AuF of the gold(I) halides is unknown in the solid state; its stability can be examined by means of a Born–Haber cycle, assuming that it would have an ionic lattice like AgF. (AuF has been generated in the gas phase from Au^+ and CH_3COF [22].)

		ΔH (kJ mol ⁻¹)
Au(s)	→ Au(g)	343.1
Au(g)	→ Au ⁺ (g) + e ⁻	890.1
$\frac{1}{2}\text{F}_2(\text{g})$	→ F(g)	79.0
F(g) + e ⁻	→ F ⁻ (g)	-322
Au ⁺ (g) + F ⁻ (g)	→ AuF(s)	-778
Au(s) + $\frac{1}{2}\text{F}_2(\text{g})$	→ AuF(s)	+212.2

Its instability relative to its constituent elements is the result of the high value of I_1 of gold and to its large enthalpy of atomization, which are not compensated for by the small lattice energy.

AuCl , AuBr and AuI are all prepared by cautious heating of Au_2X_6 ($\text{X} = \text{Cl}, \text{Br}$) or, in the case of AuI , direct synthesis

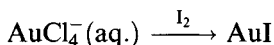
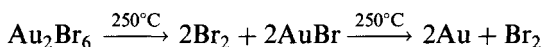
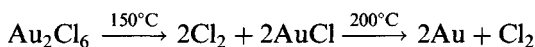


Table 4.5 Energy values^a for gold halides

		F	Cl	Br	I	Ref. ^b
AuX	ΔH	(+75)	-35	-19	1.7	1
	ΔG		-16	-15	-3.3	1
	ΔH	+212 ^c	-34.7	-13.8	0	2
AuX ₃	ΔH	-360	-121	-67.3		1
	ΔG		-54	-36		1
	ΔH	-363.6	-117.6	(-49.3) (+62.8)		2

^a All values in kJ mol⁻¹; estimated values in parentheses.

^b Data taken from:

1. R.J. Puddephatt (1978) *The Chemistry of Gold*, Elsevier, Oxford.
2. M.W.M. Hisham and S.W. Benson (1987) *J. Phys. Chem.*, **91**, 3631.

^c This book.

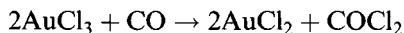
Other methods are available, especially for AuCl, such as the decomposition of Au(CO)Cl. AuCl tends to disproportionate slowly at room temperature as predicted from the data in Table 4.5.



Decomposition is rapid in solution, so that AuCl needs to be stored in an anhydrous state. All three gold(I) halides have a zig-zag chain structure (Figure 4.2) with linear coordination of gold; AuCl has a 'wide' Au-X-Au angle (93°) and AuI a narrower angle (72°), while AuBr exists in both crystalline forms.

Bond lengths are Au-Cl 2.36 Å, Au-Br 2.40–2.44 Å, Au-I 2.62 Å [23].

A compound AuCl₂ is, as might be expected from its black colour, the mixed valence Au₂^IAu₂^{III}Cl₈; it is prepared from the reaction of CO with excess AuCl₃ in SOCl₂:



The gold(I) atoms have linear coordination (Figure 4.3) and the gold(III) atoms square planar coordination [24].

There are various routes for the synthesis of the trihalides:

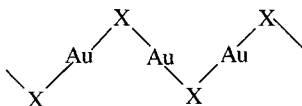
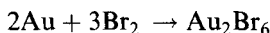
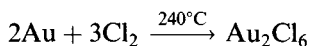
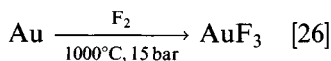
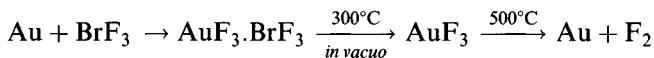


Figure 4.2 The structure of gold(I) halides in the solid state.

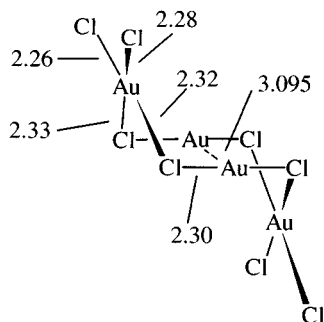


Figure 4.3 The structure of AuCl_2 .

Two structures are exhibited, both involving 4-coordinate gold, giving rise to the diamagnetism expected for square planar d^8 systems. Like AgF_3 , AuF_3 has [26] a fluorine-bridged helical structure (Figure 4.4) and is a strong fluorinating agent too.

The chloride [12] and bromide [27] are dimeric Au_2X_6 (Figure 4.5) with $\text{Au}-\text{Cl}$ 2.243–2.249 Å (terminal) and 2.334 Å (bridge); some ligands break the bridges to form adducts $\text{AuX}_3 \cdot \text{L}$ while others reduce them to gold(I) species.

Gold(III) iodide has not been definitely characterized in the solid state; substances with this formula in the solid state are probably gold(I) polyiodides Au^+I_3^- ; AuI_3 has also been detected in the gas phase (mass spectra).

The higher fluorides of gold, AuF_5 and AuF_7 , have been reported; the former is well characterized [28]:

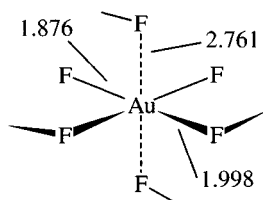
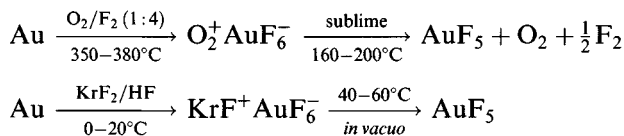


Figure 4.4 The structure of AuF_3 .

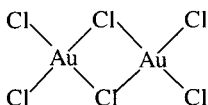


Figure 4.5 The structure of Au_2Cl_6 .

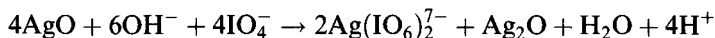
It is an intensely reactive and hygroscopic yellow–brown substance (m.p. 75–78°C); its volatility suggests a low molecular mass; Mössbauer spectra indicate 6-coordinate gold while the Raman spectrum is interpreted in terms of *cis*-bridged octahedral units. In the gas phase at 170°C, it comprises dimers and trimers [29] (electron diffraction).

AuF₇ is reported to result from the reaction of fluorine atoms (produced in a high-voltage plasma) with AuF₅ at 120–130°C, being condensed out at –196°C as a very reactive and volatile pale yellow solid (vapour pressure > 30 mmHg at room temperature) with an intense IR band at 734 cm⁻¹ (vapour). It decomposes to AuF₅ above 100°C and affords Au₂O₃ and Au on hydrolysis [18].

4.4 Oxides and other binary compounds

The main silver oxides are Ag₂O and AgO. The former is obtained as a dark brown precipitate when OH⁻ are added to solutions of Ag⁺ salts; it tends to retain traces of water and alkali, even on drying. It is basic, giving slightly alkaline solutions in water (it is a convenient mild alkali in organic chemistry) and reacting with atmospheric CO₂. On heating to 160°C, it forms silver. Isostructural with Cu₂O, it has tetrahedral coordination of silver. When fused with alkali metal oxides, mixed oxides like KAgO are formed that have Ag₄O₄⁴⁻ units with 2-coordinate silver. Analogous gold compounds are known (but not Au₂O) [30].

Black AgO is prepared by oxidation of silver salts with O₃, S₂O₈²⁻ and, most recently, SO₂/air mixtures, as well as by anodic oxidation [31]. Neutron diffraction shows it to be Ag^IAg^{III}O₂ with 2-coordinate Ag^I and square planar Ag^{III} sites. It is stable to around 100°C and gives solutions of Ag²⁺ when dissolved in dilute acid. Treatment with alkaline periodate retains the disproportionation



It finds important applications in batteries.

Less important oxides are Ag₂O₃, obtained impure by extended anodic oxidation of silver, and Ag₃O, obtained hydrothermally from Ag/AgO at 80°C, 4000 bar, which is a metallic conductor with the anti-BiI₃ structure containing an hcp array of silvers with oxide ions occupying 2/3 of the octahedral holes [32].

The only important gold oxide is brown Au₂O₃, obtained hydrated by alkaline precipitation of Au³⁺(aq.); single (ruby) crystals have been produced by hydrothermal crystallization at 235–275°C (from HClO₄/KClO₄). It has a polymeric structure [33] with square planar Au³⁺ (Au–O 1.93–2.07 Å) though with four more distant oxygens (at 2.81–3.19 Å). It decomposes to the elements on gentle heating and dissolves in strong alkali as

$\text{Au}(\text{OH})_4^-$. There have been claims for an AuO_2 , which may have been impure Au_2O_3 .

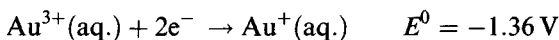
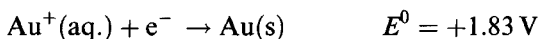
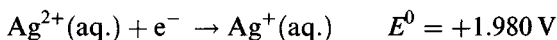
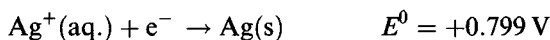
The ternary oxides M_3AuO ($\text{M} = \text{Rb}, \text{Cs}$) contain Au^- , however [34].

Other binary compounds include the very insoluble black Ag_2S ($k_{\text{sp}} \sim 10^{-51}$) and Au_2S . The latter has the cuprite structure while Ag_2S has three polymorphs; 2- and 3-coordination is found in the low-temperature form while at high temperatures Ag_2S is a conductor owing to movement of silver atoms between the framework of sulphurs. AuS and AuSe are, as would be expected, $\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{X}_2$ with digonal gold(I) and square planar gold(III) [35]; little is known about Au_2X_3 ($\text{X} = \text{S}, \text{Se}, \text{Te}$). AuTe_2 'calverite' has 4 + 2-coordination of gold by tellurium [36]. Various poly-anions such as $\text{Au}_2\text{S}_8^{2-}$, AuS_9^- and $\text{Au}_{12}\text{S}_8^{4-}$ have been made; the first two have rings with linear coordination of gold (as in $\text{Au}_2\text{Se}_5^{2-}$ and $\text{Au}_2\text{Se}_6^{2-}$) while the latter has a cube of sulphurs with golds at the middle of each edge [37]. Selenide complexes of silver [38] and gold [39] have been studied lately. Silver selenide complexes show dependence in structure on counter-ion as in $[\text{Ph}_4\text{P}\text{Ag}(\text{Se}_4)]_n$, $[\text{Me}_4\text{N}\text{Ag}(\text{Se}_5)]_n$, $[\text{Et}_4\text{N}\text{Ag}(\text{Se}_4)]_4$ and $(\text{Pr}_4\text{N})_2[\text{Ag}_4(\text{Se}_4)_3]$.

Gold forms no simple phosphide; Au_2P_3 is $\text{Au}_4^{\text{I}}(\text{P}_6^{4-})$ with $\text{P}-\text{Au}-\text{P}$ angles of 171 and 180°.

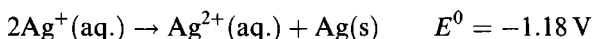
4.5 Aqua ions

Only Ag^+ and Au^{3+} are stable in aqueous solution, the latter always being complexed. The relevant potentials (in acid solution) are:



From the $\text{Ag}^+/\text{Ag}^{2+}$ potential, it is seen that the silver(II) ion is a strong oxidizing agent and is only fairly stable in strong acid; it may be prepared by ozone oxidation of Ag^+ or by reproporation of AgO (section 4.4).

Ag^+ is stable to disproportionation in aqueous solution

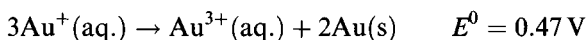


though the potential is affected by complexation and certain silver(I) macrocyclic complexes disproportionate in solution (section 4.7).

Table 4.6 Selected electrode potentials for gold(I) and gold(III) complexes $[\text{Au}(\text{L}^{n-})_2]^{(1-2n)+}$ and $[\text{Au}(\text{L}^{n-})_4]^{(3-4n)+}$

L	Gold(I) E^0 (V)	Gold(III) E^0 (V)
H ₂ O	-1.83	-1.52
Cl ⁻	-1.15	-1.00
Br ⁻	-0.96	-0.85
I ⁻	-0.66	-
SCN ⁻	-0.58	-0.64
NH ₃	-0.56	-0.33
CN ⁻	+0.61	+0.20

In the case of gold, study of the above potentials predicts correctly the disproportionation of Au⁺ in aqueous solution



For example, AuCl immediately decomposes into gold and gold(III) chloride, though some gold(I) halide complexes such as AuI₂⁻ are quite stable, while Au(CN)₂⁻ is formed by oxidation of gold in the presence of CN⁻:

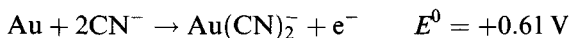


Table 4.6 shows the potentials to be ligand dependent.

X-ray scattering data on solutions of Ag⁺ indicate the presence of Ag(H₂O)₄⁺ with Ag-O about 2.4 Å [40]. Soluble silver(I) salts include AgNO₃, AgClO₄ (the periodate is insoluble), AgBF₄, AgClO₃ and AgF (all other halides are insoluble). There is no evidence for perchlorate coordination in aqueous solution. Silver nitrate is prepared from the reaction of silver with concentrated nitric acid as colourless crystals m.p. 212°C. It decomposes above 350°C to silver, oxygen, nitrogen and oxides of nitrogen. Insoluble salts of silver include the bright yellow Ag₃PO₄ and (in contrast to the chlorate) the bromate and iodate. Little is known concerning gold(III) salts such as Au(NO₃)₃.

The oxidizing power of Ag²⁺ (aqueous) is being utilized in electrochemical cells for disposal of organic wastes; solutions of Ag²⁺ in HNO₃ were originally found to be efficient oxidants for organic nuclear waste (tributyl phosphate kerosene from solvent extraction processes) but the scope has been expanded to include rubber, certain polymers, hydraulic and lubricating oils, aromatic and aliphatic hydrocarbons, organo-phosphorus, sulphur and chloro compounds (including PCBs, notoriously difficult to oxidize) [41].

4.6 Silver(I) complexes

4.6.1 Complexes of O-donors

The aqua ion as a ligand is discussed in section 4.5. Silver forms a range of light-sensitive, insoluble carboxylates that find application in the synthesis of, for example, alkyl halides and esters. The benzoate, trifluoroacetate and perfluorobutyrate have dimeric structures; others are polymers (Figure 4.6).

Commercially, the most important complexes of O-donors are the thio-sulphates, implicated in photographic 'fixing'; of several known, in $\text{NaAgS}_2\text{O}_3 \cdot \text{H}_2\text{O}$ each silver is tetrahedrally bound to three sulphurs and one oxygen while $(\text{NH}_4)_7\text{Ag}(\text{S}_2\text{O}_3)_4$ also has silver tetrahedrally bound by sulphur. Unlike other 'soft' metal ions, Ag^+ binds to Me_2SO via oxygen in $\text{Ag}(\text{DMSO})_2\text{ClO}_4$ rather than by sulphur.

4.6.2 Complexes of N-donors

Dissolution of Ag_2O in aqueous ammonia lends to the formation of $\text{Ag}(\text{NH}_3)_2^+$ ($\text{Ag}-\text{N}$ 2.110 Å in $\text{Ag}(\text{NH}_3)_2\text{SO}_4$); its reduction by aldehydes and reducing sugars is the basis of its use as Tollens' reagent, the 'silver mirror' test. In liquid ammonia, the tetrahedral $\text{Ag}(\text{NH}_3)_4^+$ is formed ($\text{Ag}-\text{N}$ 2.31 Å), isolable as a perchlorate (which loses NH_3 on keeping); silver nitrate forms $[\text{Ag}(\text{NH}_3)_3]^+\text{NO}_3^-$ with a trigonally coordinated silver ($\text{Ag}-\text{N}$ 2.281 Å) [42]. Linear coordination is formed in $\text{Ag}(\text{pyridine})_2^+\text{NO}_3^- \cdot \text{H}_2\text{O}$ ($\text{Ag}-\text{N}$ 2.26 Å, bond angle 173° ; four distant contacts to oxygens $\text{Ag}-\text{O}$ *c.* 2.9 Å); an unstable $\text{Ag}(\text{py})_4^+$ has similarly been characterized. $\text{Ag}(\text{im})_2^+$ is linear in the nitrate, but in the perchlorate, $\text{Ag}(\text{im})_2^+$ is associated in pairs (further grouped into triangular units). $\text{Ag}(\text{pyrazine})\text{NO}_3$ has silver similarly bound to two nitrogens but nitrate coordination is stronger than in the pyridine complex as the chains are kinked ($\text{N}-\text{Ag}-\text{N}$ 159°) (Figure 4.7).

An exception to the above types of structure is the cubane cluster in $(\text{AgI}(\text{piperidine}))_4$ [43].

Less study has been made of complexes with polydentate ligands. $\text{Ag}-\text{N}$ linkages have been studied in relation to polynucleotide bases and the $\text{Ag}-\text{DNA}$ interaction could be important in the use of the silver-sulphadiazine complex in burn treatment. Ethylenediamine is a bridging ligand in $\text{Ag}(\text{ClO}_4)_2$ (2-coordinate silver) but essentially planar 5-coordination

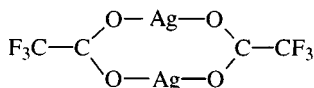


Figure 4.6 The dimeric structure adopted by some silver carboxylates such as silver trifluoroacetate.

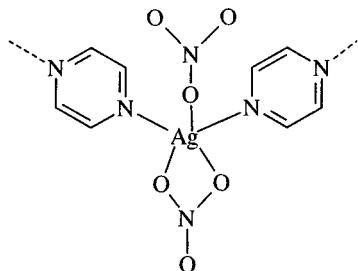


Figure 4.7 The environment of silver in $\text{Ag}(\text{pyrazine})\text{NO}_3$.

occurs in $\text{Ag}(\text{quinquepyridine})\text{PF}_6$; $[\text{Ag}(\text{PPh}_3)_2(\text{terpy})]\text{ClO}_4$ has trigonal bipyramidal coordination [44].

$\text{Ag}(4,4'\text{-bipy})\text{NO}_3$ has a three-dimensional structure with silver ions diagonally coordinated by two bipy ligands ($\text{N}-\text{Ag}-\text{N}$ 173.7°) in extended infinite chains, the chains being cross-linked by $\text{Ag}-\text{Ag}$ bonds (2.970 \AA) [45].

4.6.3 Tertiary phosphine and arsine complexes

The 1:1 phosphine complexes resemble those of copper rather than gold (Figure 4.8) [46].

More bulky phosphines favour the chair structure; $[(\text{R}_3\text{P})\text{AgX}]_4$ ($\text{R} = \text{Et}$, Ph ; $\text{X} = \text{Cl}$, Br , I) all adopt the cubane form but a second form of $[(\text{Ph}_3\text{P})\text{AgI}]_4$ has the chair structure in which some silver atoms are 3-coordinate. Some of these clusters may dissociate into dimers in solution. In contrast to the linear gold analogue, $[(\text{Ag}(\text{O}_2\text{CMe})(\text{PPh}_3))]_4$ has a tetrameric structure featuring 3- (1P, 2O) and 4- (1P, 3O) coordinate silver while a second form is dimeric $[(\text{Ph}_3\text{P})\text{Ag}(\mu\text{-O}_2\text{CMe})\text{Ag}(\text{PPh}_3)]$ with 3-coordinate silver [47]; $\text{Ag}(\text{SCN})(\text{PPR}_3^n)$ has a chain structure where 4-coordination is attained with cross-linking of $\text{Ag}-\text{S}-\text{Ag}-\text{S}$ -units. $(\text{Ph}_3\text{P})_2\text{AgX}$ ($\text{X} = \text{Cl}$, Br , I , SCN) are X-bridged dimers [48] and $(\text{Ph}_3\text{P})_3\text{AgCl}$ also features tetrahedral coordination; four tertiary phosphites, though not phosphines, can bind to one silver. Four-coordination is found in monomeric and dimeric

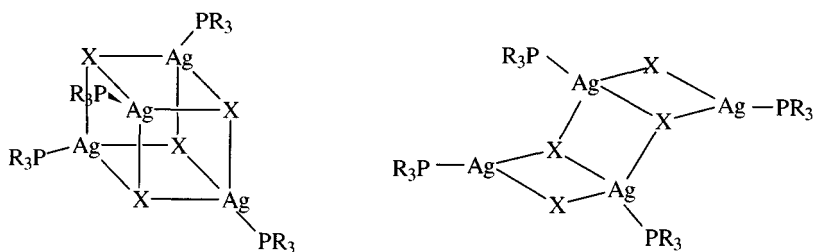


Figure 4.8 Cubane and chair structures adopted by complexes $(\text{R}_3\text{P})\text{AgX}$.

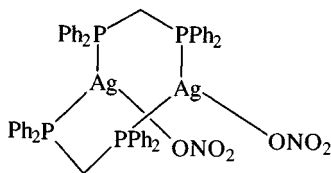


Figure 4.9 The dimeric structure adopted by $(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2\text{AgNO}_3$.

$(\text{Ph}_3\text{P})_2\text{AgNO}_3$. $[(\text{Ph}_3\text{P})_2\text{Ag}(\text{O}_2\text{CH})]$ has 4-coordinate silver with a symmetrically bidentate formate ligand [49]. Two-coordination has been established for bulky phosphines, for $[(\text{mesityl})_3\text{P}]_2\text{Ag}^+\text{PF}_6^-$ and probably for $(\text{Bu}^t_3\text{P})_2\text{Ag}^+\text{X}^-$ ($\text{X} = \text{PF}_6, \text{BF}_4, \text{ClO}_4$). Among complexes of bidentate ligands, $(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2\text{AgNO}_3$ is a dimer with 3-coordinate silver (Figure 4.9).

The series $\text{M}(\text{PP})\text{Cl}$ ($\text{PP} = 2,11$ -bis(diphenylphosphinomethyl)benzo[c]-phenanthrene; $\text{M} = \text{Cu}, \text{Ag}, \text{Au}$) is interesting in showing group trends (Table 4.7) where the silver and copper complexes have trigonal coordination and the gold member is linear [50].

Linear coordination is also found in $\text{Ag}(\text{tmpp})\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$). Bond lengths are $\text{Ag}-\text{P}$ 2.379 and $\text{Ag}-\text{Cl}$ 2.342 Å in the chloride; $\text{Ag}-\text{P}$ 2.374 and $\text{Ag}-\text{Br}$ 2.448 Å in the bromide [51a]. The 3-coordinate monomers $\text{Ag}(\text{PR}_3)(\text{CF}_3\text{COCHCOCF}_3)$ (the diketonate chelates through the two oxygens; $\text{R} = \text{Me}, \text{Et}$) are volatile and thermally stable to over 100°C; they have been suggested as CVD precursors [51b]. Four-coordination occurs in $[\text{Ag}(\text{S}_2\text{CAr})(\text{PPh}_3)_2]$ [52].

4.6.4 Complexes of halogen-donors

Silver halides dissolve in excess halide (e.g. AgCl is a hundred times more soluble in 1M HCl than in water) forming complex ions AgX_2^- and AgX_3^{2-} [53]. These isolated anions are not often found in the solid state; thus M_2AgI_3 ($\text{M} = \text{K}, \text{Rb}, \text{NH}_4$) have corner linked tetrahedra (Figure 4.10), though $\text{Au}(\text{S}_2\text{CNBu}_2)_2^+\text{AgBr}_2^-$ does have digonally coordinated silver ($\text{Ag}-\text{Br}$ 2.45 Å).

MAg_4I_5 ($\text{M} = \text{Rb}, \text{K}$) compounds are iodide-based solid electrolytes with high conductivities; the structures are based on packing of I^- , the ion Ag^+

Table 4.7 Structure of $\text{M}(\text{PP})\text{Cl}$

M	M-P average (Å)	M-Cl (Å)	P-M-P (°)
Cu	2.237	2.222	131.9
Ag	2.434	2.514	140.7
Au	2.308	2.818	175.5

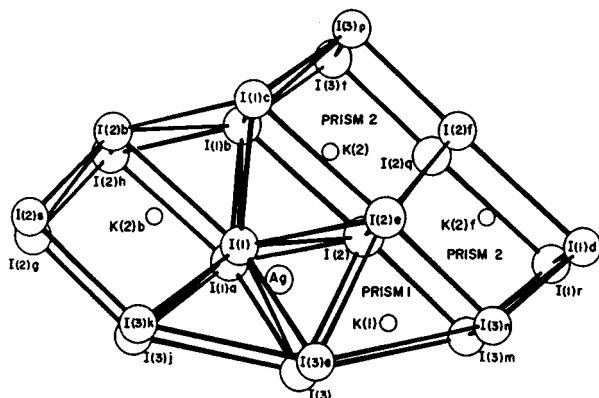


Figure 4.10 The structure of K_2AgI_3 . (Reproduced with permission from *Acta Crystallogr. Sect. B*, 1975, 31, 2339.)

(but not M^+) being mobile at room temperature, moving from one position to another with a relatively small energy barrier [54].

Trigonal coordination is also found in $M(\text{dibenzo-18-crown-6})AgX_3$ ($M = K, Rb$; $X = Cl, Br$) with $Ag-X$ bond lengths of 2.447 Å ($X = Cl$) and 2.550 Å ($X = Br$) in the rubidium salts. With the larger $K(\text{crypt-2,2,2})^+$ counter-ion, it is possible to isolate individual ions as $AgCl_2^-$. In $(PPh_3Me)^+AgI_3^-$, $Ag-I$ is 2.742–2.755 Å; $(Pr_4N)_4[Ag_4I_8]$, however, has cubane-type clusters [55].

4.6.5 Complexes of C-donors

The most important complexes with C-donors, other than organometallics, are cyanides. $AgCN$ has a structure with $Ag-C-N-Ag$ bonding in linear polymeric chains; it dissolves in excess KCN forming $K^+Ag(CN)_2^-$ (digonal with $Ag-C$ 2.13 Å, $\nu(C\equiv N)$ 2135–2139 cm^{-1}), $Ag(CN)_3^{2-}$ and $Ag(CN)_4^{3-}$ [56].

4.6.6 Complexes of S-donors

Like gold, silver readily forms insoluble (yellow) thiolates $[Ag(SR)]_n$; primary alkylthiolates are thought to have non-molecular structures but with bulky tertiary alkyls ($n \sim 8$), probably having a cyclic structure. Addition of excess thiolate leads to the formation of clusters like $Ag_6(SPh)_8^{2-}$, $Ag_5(SPh)_7^{2-}$ and $Ag_5(SBu^t)_6$ (phosphine adducts are known, too).

Octahedral silver clusters are also found in dithioacid complexes $[Ag(S_2CNR_2)]_6$ ($R = Pr, Et$) and $[Ag(S_2C=C(CN)_2)]_6^{6-}$, while $[Ag_8(S_2C=C(CN)_2)_6]^{4-}$ has a cube of silvers (Figure 4.11) [57].

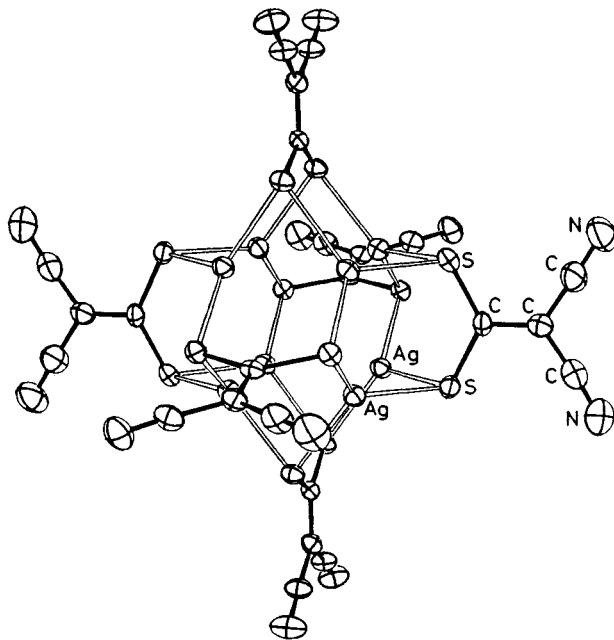


Figure 4.11 The structure of $[\text{Ag}_8\{\text{S}_2\text{C}=\text{C}(\text{CN})_2\}_6]^{4-}$. (Reproduced with permission from *J. Chem. Soc., Chem. Commun.*, 1981, 323.)

A number of thiourea complexes of silver have shown the tendency to bind up to four ligands, in contrast to gold. Thus Agtu_2X ($\text{X} = \text{Cl}, \text{NCS}$) have essentially 3-coordinate silver (one distant fourth atom); $\text{Agtu}_3\text{ClO}_4$ is a 4-coordinate dimer (Figure 4.12) [58].

Various thioether complexes have been synthesized: for example, 6-coordination is found in $[\text{Ag}(18\text{S}_6)]^+$ and $[\text{Ag}(9\text{S}_3)_2]^+$ but in $[\text{Ag}(16\text{S}_6)]^+$, tetrahedral coordination occurs, with two unused donor atoms in the ligand [59].

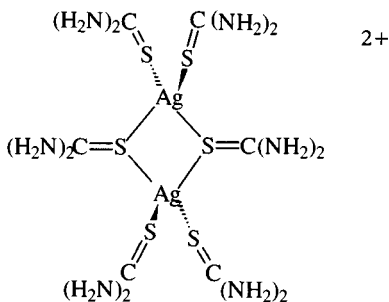
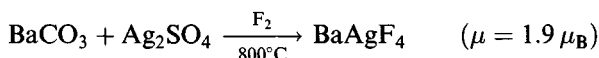


Figure 4.12 The structure of dimeric $[\text{Ag}_2(\text{tu})_6]^{2+}$ in $\text{Ag}(\text{tu})_3\text{ClO}_4$.

4.7 Silver(II) complexes

Stable compounds of silver(II) are found with N, O and F as donor atoms; macrocycles are, as elsewhere, able to support the higher oxidation state. As a d^9 system, Ag^{2+} imitates Cu^{2+} in displaying Jahn–Teller distortion.

Violet fluoro complexes like BaAgF_4 and Cs_2AgF_4 can be made by fluorination

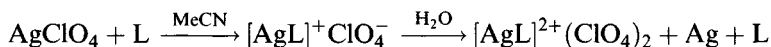


and have square planar silver ($\text{Ag–F } 2.05 \text{ \AA}$). MAgF_3 ($\text{M} = \text{K, Rb, Cs}$) and CsAgMF_6 ($\text{M} = \text{Tl, In, Sc, Fe}$) have also been made; KAgF_3 has distorted 6-coordination (perovskite structure) and CsAgFeF_6 has a compressed octahedral geometry [60].

Complexes of N-donor ligands have been made by chemical (ozone or persulphate) or electrochemical oxidation, such as $\text{Agpy}_4\text{S}_2\text{O}_8$, $\text{Ag}(\text{bipy})_2(\text{S}_2\text{O}_8)$ and $\text{Ag}(\text{bipy})_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$. Solid $\text{Ag}(\text{bipy})_2(\text{S}_2\text{O}_8)$ has $\mu_{\text{eff}} = 1.82 \mu_{\text{B}}$; $g_{\perp} = 2.032$, $g_{\parallel} = 2.134$ (in frozen solution, hyperfine structure from both silver and nitrogen are seen). $\text{Ag}(\text{bipy})_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ has distorted octahedral coordination (bidentate bipy, bridging nitrate). The value of E^0 for $\text{Agbipy}_2^+ / \text{Agbipy}_2^{2+}$ is 1.453 V, compared with 2.0 V for the aqua ion, demonstrating the ability of these ligands to stabilize higher oxidation states [61].

Picolinate and pyridine-2,6-carboxylate give stable complexes, with 4- and 6-coordination. Macrocycles like porphyrins afford silver(II) derivatives; most remarkable is the reaction of the macrocycle *meso*- $\text{Me}_6[14]\text{ane}$ (Figure 4.13).

It forms a stable silver(I) complex in acetonitrile, in keeping with the ability of MeCN to solvate Ag^+ ; in the presence of water, disproportionation occurs [62].



Silver has square planar coordination in $\text{Ag}[\textit{meso}\text{-Me}_6[14]\text{ane}](\text{NO}_3)_2$ ($\text{Ag–N } 2.16 \text{ \AA}$) with distant axial oxygens ($\text{Ag–O } 2.81 \text{ \AA}$); the complex has

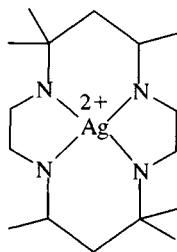


Figure 4.13 The structure of the silver(II) complex of the macrocycle *meso*- $\text{Me}_6[14]\text{ane}$.

$\mu_{\text{eff}} = 2.2 \mu_{\text{B}}$; $g_{\parallel} = 2.11$, $g_{\perp} = 2.058$. Similar complexes can be obtained with other ligands [63]; some can be oxidized, chemically or electrochemically, to silver(III) complexes.

4.8 Silver(III) complexes

As mentioned in the previous section, oxidation (with NOClO_4) of a silver(II) complex yields the yellow diamagnetic $\text{Ag}[\text{meso-Me}_6[14]\text{ane}](\text{ClO}_4)_3$; other complexes such as AgOEPClO_4 can be made; the $\text{Ag}^{3+}/\text{Ag}^{2+}$ potential is 0.44 V [64].

Fluoride complexes of silver(III) are exemplified by the purple-red Cs_2KAgF_6 (elpasolite structure, octahedral Ag^{3+} ; paramagnetic with $\mu = 2.6 \mu_{\text{B}}$). Yellow MAgF_4 ($\text{M} = \text{Na}, \text{Rb}, \text{K}$) and $\text{XeF}_5^+\text{AgF}_4^-$ are diamagnetic and probably square planar [65].

Yellow $\text{Ag}(\text{OH})_4^-$, synthesized by anodic oxidation of silver in strong alkali, is said to be stable for 2 h at 25°C in 1.2 M NaOH but decomposes to AgO and O_2 at pH 11 in 1–2 min [66].

The longest established silver(III) complexes are the red to brown biguanides, like the ethylene bis(biguanide) shown in Figure 4.14; persulphate oxidation of Ag^+ in the presence of this ligand gives a silver(III) complex with essentially square planar coordination.

4.9 Gold(-I) complexes

Gold has a high electron affinity (223 kJ mol^{-1} , compare with that for I of 295 kJ mol^{-1}) to fill the 6s subshell, because of relativistic contraction (see section 4.18). It, therefore, forms 1:1 compounds MAu with group I metals; of these Cs^+Au^- and Rb^+Au^- are ionic semi-conductors [67] with the CsCl structure ('normal' alloys of gold like those with the lighter alkali metals are metallic conductors). Au^- is also formed when gold dissolves in liquid ammonia in the presence of Cs and other alkali metals. Au^- is also found in $\text{K}_{18}\text{Ti}_{20}\text{Au}_3$, which contains $[\text{Ti}_9\text{Au}_2]^{9-}$, $[\text{Ti}_{11}]^{7-}$ and Au^- .

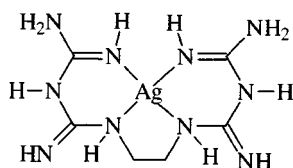


Figure 4.14 The coordination geometry of silver in the silver(III) ethylenebis(biguanide) complex.

4.10 Gold(I) complexes

4.10.1 Complexes of O-donors

Few studies have been made of these ligands; most complexes reported involve other supporting ligands as in $\text{Au}(\text{OSiMe}_3)(\text{PPh}_3)$ and $\text{Au}(\text{OCOR})(\text{PPh}_3)$, though an important Au–O bond is formed in $[(\text{Ph}_3\text{P})\text{Au}]_3\text{O}^+$ (section 4.17) [68]. Some air- and heat-stable alkoxides $\text{Au}(\text{OR}')(\text{PR}_3)$ ($\text{R} = \text{Ph}$ or cy ; $\text{R}' = \text{CH}_2\text{CF}_3$ or $\text{CH}(\text{CF}_3)_2$) have been reported [69].

4.10.2 Complexes of N-donors

The 'soft' Au^+ forms relatively few complexes compared with those of phosphines. Complexes with amines, nitriles and diazoles like $\text{Au}(\text{NH}_3)_2^+$ and $\text{Au}(\text{RCN})_2^+$ are known but little studied. In linear $\text{Au}(\text{NH}_3)_2^+$, Au–N is 2.01–2.03 Å [70a]. $[\text{Au}(\text{NCPh})_2]^+$ has been used as a labile source of other gold complexes [70b]. $\text{AuCl}(\text{piperidine})$ is a monomer with weak tetrameric association; in contrast $\text{AuX}(\text{py})$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) are $[\text{Aupy}_2]^+[\text{AuX}_2]^-$ with a chain structure in the solid state (and Au–Au interactions), suggesting a close balance between factors for 'molecular' and ionic structures [70c] (note also the tetrahydrothiophene complexes in section 4.10.6).

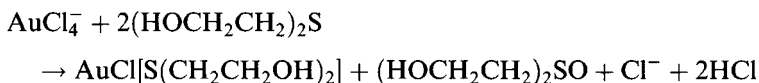
4.10.3 Tertiary phosphine and arsine complexes

The phosphine and arsine complexes of gold(I) have been intensively studied since the early 1970s. The possibilities of coordination numbers between 2 and 4 have been explored, though the use of bulky ligands is less essential than with the isoelectronic $\text{M}(\text{PR}_3)_2$ ($\text{M} = \text{Pd}, \text{Pt}$) compounds and the coordination numbers depend on both steric and electronic factors [71].

The usual starting material is AuCl_4^- , which can be reduced with the tertiary phosphine



or more cheaply, *in situ* with 2,2'-thiodiethanol, (bis-2-hydroxyethylsulphide)



or via an isolable complex with a weakly bound ligand like tht, the intermediate being reacted with the tertiary phosphine (or arsine)



1:1 complexes

X-ray diffraction shows linear coordination in $(\text{Ph}_3\text{P})\text{AuX}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NO}_3, \text{SCN}$ [72], Ph [73], SR [74], $\text{CN}, \text{Me}, \text{CF}_3$ [75] OCOMe [76],

Table 4.8 Au–P bond lengths in the 2-coordinate complexes (Ph₃P)AuX

Donor atom	X	Au–P (Å)
O	NO ₃	2.199
	OCOMe	2.207
	OCOCF ₃	2.208
	OCOCHCl ₂	2.210
	OCOPr ⁱ	2.213
	SO ₄	2.216
	OCOCH(OH)Me	2.219
N	NCO	2.222
	NMe ₃	2.231 (ClO ₄ salt)
Cl	Cl	2.235
Br	Br	2.252
I	I	2.249
S	SCN	2.252
	SPh	2.259
	S ₂ COEt	2.260
	S ₂ COMe	2.261
	S ₂ CPh	2.263–2.269
C	CNO	2.274
	C ₆ F ₅	2.27
	C≡CC ₆ F ₅	2.274
	Me	2.279
	CN	2.278
	(2,6-MeO) ₂ Ph	2.284
	CF ₃	2.285
	Ph	2.296
P	PPh ₃	2.295 (C(CN) ₃ salt)
	PPh ₃	2.311 (NO ₃ salt)
	PPh ₃	2.312 (PF ₆ salt)
	PPh ₃	2.325 (solution)

OCOCF₃, S₂CNEt₂, S₂COMe [77], OCOPh, NMe₃ [78], etc.), R₃PAuCl [79] (R₃ = cy₃, Phcy₂, Me₃P, Et₃P, Cl₃P, (PhO)₃P and (tolyl)₃P), Pr₃PAuC₅H₅ and Ph₃AsAuX (X = Cl, Br). In all of these the ligand X is monodentate (note the monodentate nitrate and dithio ligands, as well as the monohaptocyclopentadienyl). Table 4.8 shows the *trans*-influence of the ligand X on the Au–P bond length in some of these compounds; it depends on the donor atom in X rather than X itself, the bond lengths following a trend in agreement with *trans*-effect orders.

Complexes other than the chloride are prepared by a variety of reactions, including metathesis and re-distribution:

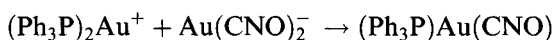
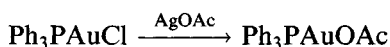
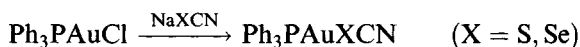


Table 4.9 Structure and spectroscopic data for AuX(tmpp)

X	Au-P (Å)	Au-X (Å)	$\nu(\text{Au-X})$ (cm ⁻¹)
Cl	2.253	2.303	313
Br	2.255	2.413	218
I	2.239	2.586	183

PF₃AuCl, prepared from Au₂Cl₆ and PF₃ in SOCl₂ has a vapour pressure of 10⁻⁴ mbar at room temperature and has been suggested as a laser CVD precursor [80].

The series AuX(tmpp) shows clear patterns [81] in structure and spectroscopic parameters (Table 4.9) (X = Cl, Br, I).

Complexes with more than one phosphine

The 2 : 1, 3 : 1 and 4 : 1 complexes have been prepared by altering the stoichiometry of the reaction mixture; the complex formed in solution depends on the cone angle of the phosphine (as with M(PR₃)_n (M = Pd, Pt)) [71]. Thus PBu₃^t and Pcy₃ form only 2 : 1 complexes (three Pcy₃ can bind to the larger Pt) whereas PBu₃ⁿ forms 3 : 1 complexes and with PEt₃, up to 4 : 1 complexes can be obtained. The stoichiometry of the complex isolated in the solid state depends on factors such as the coordinating power of the anion present and upon the balance between cation and anion size. Thus (PPh₃)₂AuSCN is 3-coordinate, but because of the bulk of tricyclohexylphosphine, (cy₃P)₂Au⁺SCN⁻ is 2-coordinate [82].

Many structures have been determined including (PPh₃)₂Au²⁺X⁻ (X⁻, e.g. NO₃, PF₆, C(CN)₃) [83], (Pcy₃)₂Au⁺X⁻ (X = NCS, PF₆, Cl) [79], (PPh₂Me)₂Au⁺PF₆⁻, (Bu₃P)₂Au⁺BPh₄⁻ [84] (all are linear, 2-coordinate); (PPh₃)₂AuX (X = Cl, Br, I, NCS) and (PPh₃)₃Au⁺X⁻ (X = BPh₄) are 3-coordinate and (PPh₃)₃AuX (X = Cl, SCN), (PPh₂Me)₄Au⁺PF₆⁻, (PPh₃)₄Au⁺BPh₄⁻ and (SbPh₃)₄Au⁺ClO₄⁻ [85] are 4-coordinate. The 3-coordinate complexes are essentially trigonal when all the ligands are the same, or slightly distorted in (PPh₃)₂AuX, where steric effects force the P-Au-P angle to exceed 120° [86]. The 4:1 complexes are distorted tetrahedra [85]. 'Mixed' 3-coordinate complexes like [(PPh₃)Au(bipy)]⁺ have been made [87], with very asymmetric bidentate coordination (Figure 4.15).

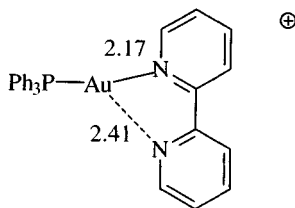
**Figure 4.15** The asymmetric coordination geometry in [(Ph₃P)Au(bipy)]⁺.

Table 4.10 Bond lengths (Å) in the complexes $(PPh_3)_nAuX$ and $(PPh_3)_2AuX$

$(PPh_3)_nAuCl$			$(PPh_3)_nAuSCN$			$(PPh_3)_2AuX$		
<i>n</i>	Au–P	Au–Cl	<i>n</i>	Au–P	Au–S	X	Au–P	Au–X
1	2.235	2.279	1	2.252	2.304	Cl	2.27	2.533
2	2.27	2.533	2	2.348	2.469	Br	2.323	2.625
3	2.41	2.71	3	2.396	2.86	I	2.333	2.754

Trends in Au–X and Au–P bond lengths in complexes $(PPh_3)_nAuX$ should be noted (Table 4.10); the Au–Cl bond length varies more with changes in coordination number than does the Au–P bond and is, therefore, more sensitive to the decrease in *s* character as the hybrid orbitals used by gold change from sp^3 .

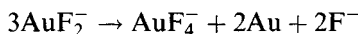
Luminescence has been noted [88] in numerous gold phosphine complexes.

Rather fewer complexes with polydentate ligands have been studied [89]. Interest in possible use of $Au(dppe)_2^+$ in cancer therapy has led to the determination of the structures of $(AuCl)_2dppe$ and $Au(dppe)_2^+X^-$ ($X = Cl, SbF_6$). The former has the diphosphine acting as a bridging ligand while the latter has a tetrahedral cation as in $[Au(1,2-(Me_2As)_2C_6H_4)_2]^+$. The compound $[Au(PP)]Cl$ has already been referred to in section 4.4 as an example of the preference of gold for 2-coordination [50].

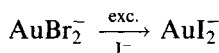
The tridentate $MeC(CH_2PPh_2)_3$ gives $MeC(CH_2PPh_2AuCl)_3$.

4.10.4 Complexes of halogen-donors

The ions AuX_2^- ($X = Cl, Br, I$) are well known; the chloride and bromide are particularly unstable in water unless excess halide ion is present. Although AuF does not exist as a solid (section 4.3.2), it has been suggested that the unknown AuF_2^- could be stabilized by ions such as Ph_4As^+ to prevent the disproportionation:



The series Bu_4NAuX_2 have been prepared by reactions like

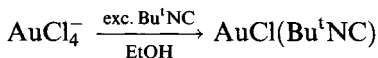
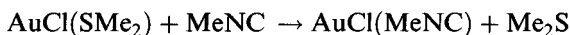


Au–X bond lengths in the series are 2.257 Å (Cl), 2.376 Å (Br) and 2.529 Å (I); they are affected by counter ions, Au–Cl being 2.281 Å in $Cs_2AuCl_2AuCl_4$. AuX_2^- exhibits Au–X stretching vibrations in the IR at 350, 254 and 210 cm^{-1} ($X = Cl, Br, I$, respectively, in the Bu_4N salts) and in Raman spectra at 329, 209 and 158 cm^{-1} , respectively [90].

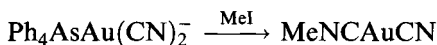
Ions of the type AuX_2^- are found as counter ions in other complexes like $\text{Aupy}_2^+ \text{AuCl}_2^-$, $\text{Au}(\text{Bu}_2\text{NCS}_2)_2^+ \text{AuBr}_2^-$ and $\text{Au}(\text{tht})_2^+ \text{AuI}_2^-$.

4.10.5 Complexes of C-donors

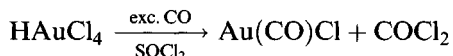
AuCN has a similar structure to AgCN and likewise dissolves in excess cyanide to form $\text{Au}(\text{CN})_2^-$; this is important in the extraction of gold. It has been characterized as various salts (Tl, K, Bu_4N , Cs) with $\text{Au}-\text{C}$ 1.964 Å (Bu_4N salt [91]). The thallium salt has short $\text{Au}-\text{Au}$ (3.10 Å) and $\text{Au}-\text{Tl}$ (3.50 Å) interactions; extended-Hückel calculations indicate the importance of relativistic effects in these covalent interactions. Isocyanides form stable complexes:



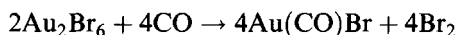
The latter is linear with a short $\text{Au}-\text{C}$ bond (1.92 Å); excess isocyanide lends to $\text{Au}(\text{RNC})_2^+$ and possibly $\text{Au}(\text{RNC})_4^+$. An unusual synthesis is



The linear $\text{Au}(\text{CO})\text{Cl}$ ($\nu(\text{C}-\text{O})$ 2153 cm^{-1}), useful as a synthetic intermediate, is prepared by [92]



$\text{Au}(\text{CO})\text{Br}$ has been obtained in solution (only)



while $\text{Au}(\text{CO})_2^+$ has been isolated in various salts (section 4.16.1).

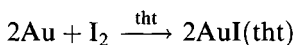
4.10.6 Complexes of S-donors

The most important complexes of S-donors are thiolates, simply regarded as $[\text{Au}(\text{SR})_n]$, long used for treatment of rheumatoid arthritis (section 4.20). Little is known about their structures: it has been remarked that their clinical use would be unlikely to be sanctioned were they currently undergoing trial. EXAFS and Mössbauer measurements indicate that they have digonal coordination of gold ($\text{Au}-\text{S} \sim 2.30$ Å) and are, therefore, thiolate-bridged polymers [93a]. Hexameric structures have been suggested for some complexes with long alkyl groups that are soluble in organic solvents and have been established crystallographically for $\text{R} = 2,4,6\text{-Pr}_3\text{C}_6\text{H}_2$, which has a 12-membered Au_6S_6 ring in a chair configuration [93b]. Linear $\text{Au}(\text{SH})_2^-$ is obtained from $\text{Au}(\text{acac})_2^-$ and H_2S ($\text{Au}-\text{S}$ 2.277–2.297 Å) [94]. Reaction with phosphines affords monomeric R_3PAuSR (e.g. auranofin);

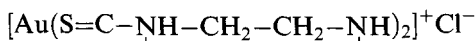
the anion in $\text{Ph}_4\text{As}^+\text{Au}(\text{SPh})_2^-$ [95] contains digonally coordinated gold ($\text{Au}-\text{S}$ 2.262–2.271 Å) while in $\text{Au}(\text{SR})_2^-$ ($\text{R} = 2,4,6\text{-Pr}_3\text{C}_6\text{H}_2$) $\text{Au}-\text{S}$ is 2.288 Å [93].

Linear $\text{S}-\text{Au}-\text{S}$ (but non-linear $\text{Au}-\text{S}-\text{C}$) is found in $\text{PhAs}^+\text{Au}(\text{SCN})_2^-$ [96]; related phosphine complexes $(\text{R}_3\text{P})_n\text{AuSCN}$ have been made (section 4.10.3). Sulphate and thiosulphate bind through sulphur; $\text{Na}_3\text{Au}(\text{S}_2\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$ has linear 2-coordinate gold in contrast to tetrahedral coordination of silver by sulphur and oxygen.

Among neutral ligands, thioethers form important complexes $\text{AuCl}(\text{SR}_2)$ (SR_2 , e.g. Me_2S , Et_2S , $\text{S}(\text{CH}_2\text{CH}_2\text{OH})_2$) that are synthetically useful since the sulphide is readily replaced by strong donors (e.g. tertiary phosphines) (sections 4.10.3 and 4.10.5). $\text{AuX}(\text{tht})$ ($\text{X} = \text{Cl}$, I) have been made. The iodide is $\text{Au}(\text{tht})_2^+\text{AuI}_2^-$, but the chloride and bromide are neutral $\text{AuX}(\text{tht})$. The iodide remarkably can be synthesized at room temperature [97]:



Essentially linear coordination is found in thiourea complexes $\text{AuBr}(\text{S}=\text{C}(\text{NR}_2)_2)$ ($\text{R} = \text{H}$, Me) and



Bidentate dithiolate ligands afford complexes like $\text{Au}(\text{S}_2\text{CNR}_2)$ ($\text{R} = \text{Et}$, Pr , Bu) and $\text{Au}(\text{S}_2\text{PR}_2)$ ($\text{R} = \text{Pr}$), which have dimeric structures based on 8-membered rings with linear $\text{S}-\text{Au}-\text{S}$ coordination and short $\text{Au}-\text{Au}$ distances. These in turn are associated into chains (Figure 4.16) ($\text{Au}-\text{Au}$ c. 3.0–3.4 Å) [99].

The dithioacetate is a tetramer, still with digonally coordinated gold [100]. Though long known, the gold complexes of terpenethiolates ('liquid gold')

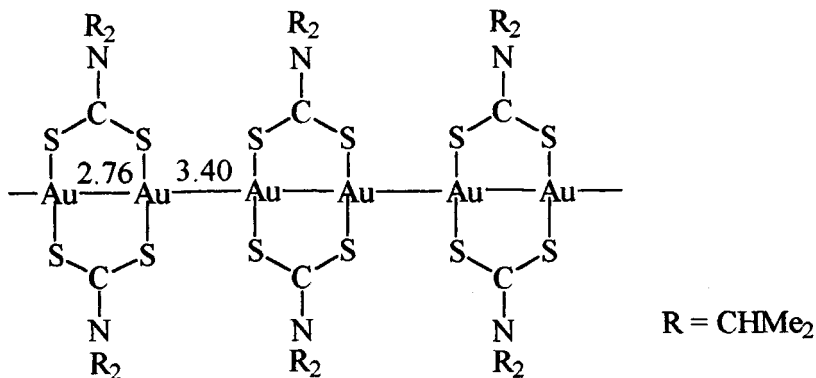


Figure 4.16 The structure of $\text{Au}(\text{S}_2\text{CNPt}_2)$ showing the association of dimeric units into chains.

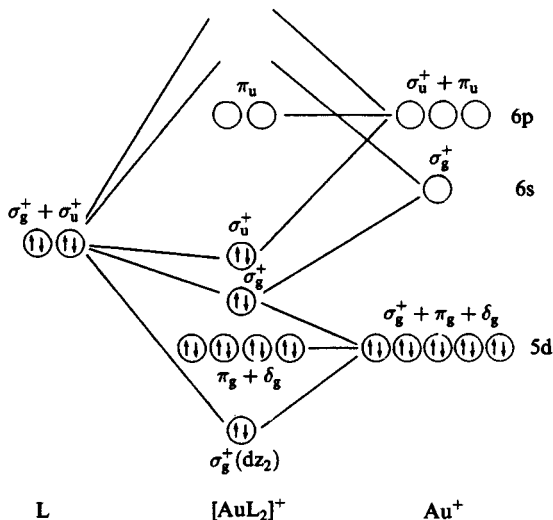


Figure 4.17 A qualitative molecular orbital scheme for a σ -bonded complex ion $[\text{AuL}_2]^+$. (Reprinted with permission from *Inorg. Chem.*, 1982, **21**, 2946. Copyright (1982) American Chemical Society.)

have, as yet, unknown structures; when painted on to pottery, then fired, they decompose to give a gold film.

4.10.7 MO schemes for 2-coordinate gold(I) complexes

A typical scheme [101] for a complex AuL_2^+ is shown in Figure 4.17.

A simple crystal field treatment predicts

$$5d_{z^2}(\sigma) > 5d_{xz, yz}(\pi) > 5d_{xy}, d_{x^2 - y^2}(\delta),$$

the latter expected to be essentially non-bonding, but the relative energies will be ligand dependent, with electronegative ligands increasing d orbital participation and more electropositive ligands increasing s/p participation. There will also be gold 6s and 6p mixing into the highest ligand-field orbitals. Analysis of the spectra of $\text{Au}(\text{CN})_2^-$ gave the ordering $d_{z^2}(\sigma) > d_{xy}, d_{x^2 - y^2}(\delta) > d_{xz}, d_{yz}(\pi)$ whereas the PE spectrum of $(\text{Me}_3\text{P})\text{AuMe}$ was interpreted in terms of $d_\pi \sim d_\delta > d_\sigma$. MO calculations for AuX_2^- (X = F to I) have recently indicated $d_\delta > d_\pi > d_\sigma$ [96].

4.11 Gold(II) complexes

Unstable dithiocarbamates $\text{Au}(\text{S}_2\text{CNR}_2)_2$ have been detected in solution by ESR but the square planar $\text{Au}(\text{S}_2\text{C}_2(\text{CN})_2)_2^{2-}$ has been isolated as a green Bu_4N^+ salt; the gold(II) state appears to be stabilized by delocalization of