Heteronuclear Metal−Metal Contacts between Gold(I) and Group-11, -12, and -13 Centers

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Closed-shell interactions occur mainly for some heavy late transition metals and main-group elements. In fact, these are dispersion forces reinforced by relativistic effects and by ionic components, of which the former are maximized in heteronuclear interactions. Heteronuclear compounds containing gold(I) and group-11, -12, and -13 metals display d^{10}–d^{10} or d^{10}–s^2 closed-shell interactions of intermediate strength relative to the homonuclear metal–metal interactions. The number of examples of gold(I)–gold(I) contacts is large, but representatives of heteronuclear gold(I)–metal contacts are still scarce. There are two general types of derivatives displaying short gold–metal distances: those with bridging ligands and those with unbridged ones, of which the latter are always the more indicative of the presence of a real bond. Derivatives featuring unsupported gold–metal bonds have been obtained mainly through reactions between basic gold(I) complexes and acid complexes, and also by encapsulation of metal centers in metallocryptands. Most derivatives with supported gold–metal bonds have been synthesized by use of C-donor ligands or ambidentate ligands. The gold–metal contacts dramatically affect the conformations and the aggregation of the molecules, and also their optical properties. Some of these derivatives are, in fact, intensely luminescent.

1. Introduction

Closed-shell species with opposite electric charges form strong ionic bonds, but such bonds should not be expected if their charges are similar. However, it has been shown experimentally that such closed-shell interactions do occur, mainly for some heavy late transition metals and main-group elements; these interactions are weaker than ionic bonds but stronger than other van der Waals bonds.[1]

The most typical case is found in gold(I) chemistry, and the term aurophilicity was coined by Schmidbaur to refer to this phenomenon. Linear two-coordinate gold(I) compounds with d^{10} configurations tend to associate into dimers, oligomers, or polymers through gold−gold contacts, showing gold−gold distances in the 2.69−3.35 Å range. The energies associated with these aurophilic interactions go from 20 to 50 kJ/mol, close to those found in hydrogen bonds.[2−4] Aurophilicity has been used in crystal engineering of homo- and heterometallic systems to design supra-

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MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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molecular structures, because it affects molecular conformations and intermolecular aggregation.[5−7]

Similarly, the terms cuprophilicity (Cu−Cu < 2.8 Å) and argentophilicity (Ag−Ag < 3.4 Å) have been used to describe this phenomenon in the cases of copper and silver, respectively, the energies involved being lower than in the case of gold but close to those of standard van der Waals interactions. The same phenomenon was also found for the close heavy metals mercury, thallium, and platinum; it was again less energetic, although some small contributions from metal−metal bonding could not be ignored.[1,8,9] Curiously, the first direct observation of a d orbital was achieved in charge-density maps of cuprite (Cu_2O), thanks to the hole in the d^{10} configuration due to Cu^I-Cu^I interactions.[10,11]

Great efforts have been devoted to theoretical studies trying to explain this phenomenon by different approaches. Pyykkö and co-workers have concluded that the aurophilic attraction is an electronic correlation effect strengthened by the relativistic effect, which has a maximum for gold. They extended their studies to other closed-shell metallic interactions in d^{10}, d^8, or s^2 systems and also to mixed systems; the term metallophilic attraction was coined to describe this phenomenon. From these, it is a dispersion force reinforced by relativistic effects (for heavy atoms) and by ionic components, the former already being important for gold−gold interactions but being more clearly seen for heteronuclear interactions.[1,12−15]

Heteronuclear compounds containing gold(I) and group-11, -12, and -13 metals display $d^{10}-d^{10}$ or $d^{10}-s^2$ closed-shell interactions of intermediate strength relative to the homonuclear metal−metal interactions. The natures of the ligands and competition with other weak forces, such as hydrogen bonds or π−π interactions between aromatic rings, play an important role. It is important to note that these interactions are invoked for copper−, silver−, mercury−, indium−, and thallium−gold distances shorter than the sums of the corresponding van der Waals radii (3.06, 3.38, 3.21, 3.59 and 3.62 Å, respectively; values taken from Table 3 in ref.[1]) and are regarded as strong if they are less than or close to the sums of the metallic radii (2.72, 2.89, 3.04, 3.07 and 3.14 Å, respectively).[16]

Three general strategies are used to build these heteronuclear compounds: a) supported gold−metal bonds in which bridging ligands are present, b) unsupported gold−metal bonds through reactions between basic/donor gold(I) complexes and acid/acceptor complexes to give acid−base/acceptor−donor stacking, and c) unsupported gold−metal bonds by encapsulation of a metal center of a dinuclear gold(I) cryptand.

Moreover, there are gold−metal clusters in which the metallic centers can be formally considered to be in an oxidation state between 0 and 1, and display similar or shorter gold−metal distances. In the same kind of clusters, $Au(PR_3)^+$ fragments can be added or scrambled to give a mixture of $Au(PR_3)^+$ and $M(PR_3)^+$ (M = Cu, Ag) units. These have been reviewed elsewhere and are not considered here, at least for clusters bigger than heptanuclear.[17−19]

The metal−metal contacts dramatically affect the conformations and the aggregation of the molecules, as happens in the most typical case of aurophilicity, and this in turn affects some properties, such as the optical properties.[20] The optical properties of these derivatives (generally gold or platinum compounds) have applications in sensor technology,[21,22] and they have been used to detect oxygen,[23] volatile organic compounds,[24,25] potassium,[26] or phosphane[27] in solution, whilst other display solvoluminescence.[28] Similarly, some results for gold−silver derivatives have recently been obtained.[29]

The number of examples of gold(I)−gold(I) contacts is large, but examples of the heteronuclear gold(I)−metal contacts are still scarce. In this microreview we summarize the state of the art in heteronuclear metal−metal contacts of gold(I) with group-11, -12, and -13 centers − mainly with silver(I) and thallium(I) − for which the gold−metal distances have been determined and show the presence of $d^{10}-d^{10}$ or $d^{10}-s^2$ closed-shell interactions.

The microreview is organized as follows:

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2. Derivatives with Unsupported Gold−Metal Bonds

The clearest cases of metal−metal bonding are produced by the presence of short metal−metal distances in the absence of bridging ligands. In such cases, the gold−metal contacts produce aggregation, which usually dramatically affects the optical properties. Some heteronuclear derivatives, for instance, become luminescent after formation of the gold−metal bond. These derivatives can be obtained mainly by two approaches: 1) by use of bis(halophenyl)aurate(I) or trinuclear cyclic gold(I) complexes as a base, therefore maximizing the electrostatic component of these closed-shell interactions, and 2) by encapsulation of a metal center by a dinuclear gold(I) cryptand.

2.1. With Bis(halophenyl)aurate(I) Salts as Bases

Because of the number of examples, we divide this section into two parts: one for silver derivatives, and the other for thallium derivatives, the latter being prepared by the same type of reaction.

2.1.1. Unsupported Gold−Silver Contacts

In 1981 we characterized the first example of such a gold(I)−silver(I) interaction in a chain polymer containing the moiety $[(C_6F_5)_2Au(\mu\text{-}AgSC_4H_8)_2Au(C_6F_5)_2]_\infty$, with Ag−Au acceptor−donor (or acid−base) bonds based on dispersive and electrostatic attraction between their metal centers.[30] There is a rhomboidal arrangement of the four metallic centers, in which the gold−silver distances are as short as 2.718(2) and 2.726(2) Å, whilst the inter-unit gold−gold distance is 2.889(2) Å; for the analogue with benzene (η^2-bonded symmetrically to the silver center) in place of tetrahydrothiophene (SC_4H_8) the gold−silver distances are 2.702(2) and 2.792(2) Å, and the gold−gold distance is 3.013(2) Å (see Figure 1).[31] Therefore, the gold−silver contacts are shorter than the gold−gold contacts in these compounds.

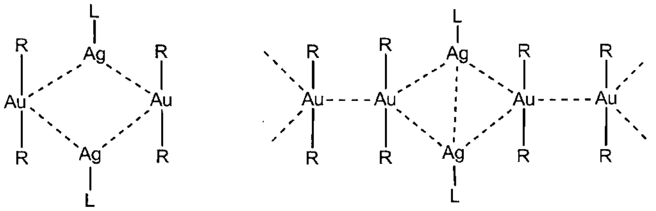

Figure 1. Complexes $[R_2Au(\mu\text{-}AgL)_2AuR_2]$ with rhomboidal geometry and unsupported gold−silver bonds; additional inter-unit gold−gold and intramolecular silver−silver contacts are possible

The basic aurate anion reacts with silver(I) to give a yellow solution. From this, through addition of ligand, yellow or orange polymers ($[R_2Au(\mu\text{-}AgL)_2AuR_2]_\infty$) are available with a variety of O-, N-, S-, or P-donors as auxiliary ligands, and R being a halophenyl ligand (R = C_6F_5, $C_6F_3H_2$ or C_6Cl_5). By this method, 35 different complexes have been prepared. These complexes are only soluble in coordinating solvents, but color loss is related to the cleavage of the gold−gold bonds.

Chain formation can be avoided by the use of bulky ligands at the gold centers, preventing aggregation through gold−gold interaction. We have thus synthesized the neutral or cationic tetrametallic phosphorus ylide gold−silver complexes $[(R_3PCH_2)_2Au(\mu\text{-}AgL)_2Au(CH_2PR_3)_2]$ (PR_3= PPh_3, PPh_2Me, $PPhMe_2$; L = $OClO_3$, PPh_3). X-ray diffraction studies carried out for L = PR_3 = PPh_3 show short gold−silver distances of 2.760(2) and 2.783(2) Å, within the previously observed range for these unsupported contacts, but there are no gold−gold interactions.[32]

We have recently revisited these polymeric derivatives in order to study their optical properties, because aggregation through gold(I)−gold(I) interactions has a dramatic effect on these properties in solution and in the solid state.[33] The absorption and emission spectra of $[(C_6F_5)_2Au(\mu\text{-}AgOCMe_2)_2Au(C_6F_5)_2]_\infty$ in acetone are consistent with molecular aggregation through gold−gold interactions when this compound goes from dilute solution conditions to concentrated ones. This derivative is also strongly luminescent in the solid state (546 nm at room temperature and 554 at 77 K). DFT calculations agree with the experimentally observed behavior and show the natures of the orbitals involved in each transition. In fact, the emission is attributable to pentafluorophenyl $\pi\pi^*$ excited states or π-MMCT transitions in dilute solutions and to metal-centered excited states in concentrated solutions or in the solid state. Moreover, the gold−silver distances in this derivative are 2.7829(9) and 2.7903(9) Å; the gold−gold distance is 3.1674(11) Å, which is different from the previous structures. There is also a short silver−silver distance of 3.1810(13) Å.

By the same strategy, we have prepared a polymeric chain containing the dinuclear moiety $[Ag(py)_3][Au(C_6F_5)_2]py$ rather than a tetranuclear one. An X-ray study showed disorder in the silver atom position, but the geometry was confirmed. Theoretical calculations reveal the presence both of metallophilic gold−silver (with ionic and dispersion contributions) and of aromatic pentafluorophenyl−pyridine interactions (dispersion effect).[34]

2.1.2. Unsupported Gold−Thallium Contacts

In 1998 we characterized the first extended unsupported gold−thallium linear chain containing the $[Tl(OPPh_3)_2][Au(C_6F_5)_2]$ moiety, with gold−thallium distances of 3.0358(8) and 3.0862(8) Å (Figure 2).[35] It was synthesized in the same way as the gold−silver polymers, through the reaction between the electron-rich $[Au(C_6F_5)_2]^-$ anion and a thallium salt in the presence of ligand.

In the same manner, we also prepared $[Tl(OPPh_3)][Tl(OPPh_3)L][Au(C_6Cl_5)_2]_2$ (L = THF, acetone), which also displayed extended unsupported chains with short gold−thallium distances, in the 3.0529(3)−3.3205(3) or 3.0937(3)−3.2705(4) Å ranges for tetrahydrothiophene or acetone, respectively (Figure 2).[36] Moreover, the thallium centers show two different types of geometrical environments, such as pseudotetrahedral and distorted trigonal-bi-

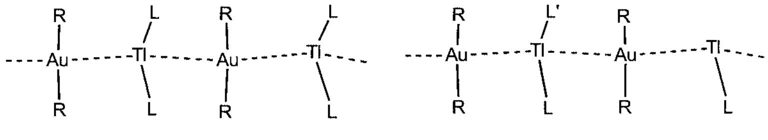

Figure 2. Asymmetric unit of linear chains with unsupported gold−thallium bonds; left: L = $OPPh_3$, R = C_6F_5; right: L = $OPPh_3$, L′ = THF, acetone; R = C_6Cl_5

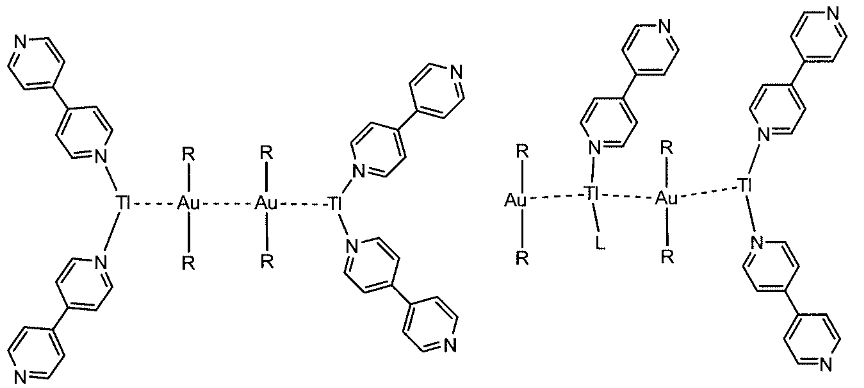

Figure 3. Tetranuclear moieties, further linked to others through bipy bridging ligands to give two-dimensional polymers; left: R = C_6F_5; right: L = THF, R = C_6Cl_5

pyramidal, due to the presence of solvent molecules that act as ligands in the solid state. Ab initio calculations, performed for the model $[Tl(OPH_3)_2][Au(C_6H_5)_2]$, are consistent with the presence of a high ionic contribution (80%) and a dispersion type with a charge-transfer contribution (20%). These three derivatives emit at 494, 497, and 501 nm, respectively, in the solid state at room temperature. Moreover, the last two derivatives show site-selective excitation at 77 K, which could be related to the different environments around the thallium centers. In fact, TD-DFT (density functional level by the time-dependent perturbation theory approach) calculations were in agreement with the experimental excitation spectra for all complexes and confirm the qualitative explanation that the excitation has $AuR_2 \rightarrow Tl$ charge-transfer character, whereby the thallium centers act as fluorophores. Again, the polymer structure is lost in donor solvents, so the colored crystals became uncolored in solution and do not luminesce.

Similar reactions resulted in the synthesis of the tetranuclear derivatives $[Tl(bipy)]_2[Au(C_6F_5)_2]_2$ (bipy = 4,4′-bipyridine) and $[Tl(bipy)][Tl(bipy)_{0.5}(THF)][Au(C_6Cl_5)_2]_2$.[37] In the first compound, a strong unsupported gold−thallium interaction of 3.0161(2) Å is found, together with gold−gold contacts of 3.409(3) Å, to give an unusual linear Tl−Au−Au−Tl arrangement in which repulsive instead of attractive forces might be expected {this non-fulfillment of the Coulomb rule was also observed[38] in $[Au(PPhMe_2)_2][Au(GeCl_3)_2]$, with the same unusual + − − + sequence}. The tetranuclear moiety is further linked through bidentate bridging bipy ligands (one bipy ligand bridging two thallium centers in two different moieties) to give a two-dimensional array. Finally, adjacent planes are connected through two additional Tl−F contacts to form an infinite three-dimensional polymer. The second compound displays a Tl−Au−Tl′−Au arrangement with two short gold−thallium distances of 3.0323(4) and 3.0540(4) Å and, again, bidentate bridging bipy ligands to form a two-dimensional polymer (Figure 3). Both complexes are strongly luminescent at room temperature, losing this property in solution (even in concentrated solutions), and so the luminescence is attributed to interactions between metal atoms. TD-DFT calculations agree with this proposal, and the obtained theoretical excitation spectra match the experimental results.

A similar reaction, however, carried out without addition of any ligand other than the solvent, produced the derivative $[Au_2Tl_2(C_6Cl_5)_4](OCMe_2)$, the crystal structure of which consists of a tetranuclear unit with four short unsupported gold−thallium contacts within the 3.0331(6)−3.1887(6) Å range and a longer thallium−thallium interaction of 3.6027(6) Å (Figure 4).[39] Two $[Au(C_6Cl_5)_2]^-$ units are held together by two thallium centers in a butterfly geometry, reminiscent of the silver−gold tetranuclear structures with unsupported gold−silver bonds, but now without additional gold−gold bonds; in addition to this, the thallium atoms show weak interaction with the oxygen atom of an acetone molecule. This complex luminesces at 556 nm at room temperature in the solid state, with lifetimes in the order of microseconds. Moreover, the starting materials do not luminesce, so this phenomenon could be assigned to the metal−metal bonds. Unlike in the case of other unsupported gold−thallium bonds, the structure of this complex is maintained in solution, in which it luminesces and shows solvent dependence. TD-DFT calculations carried out for $[Au_2Tl_2(C_6H_5)_4]$ show that the orbital from which the emission is produced is almost completely based on the two thallium(I) atoms, so these are therefore perturbed in solution by the presence of solvent molecules with donor capabilities.

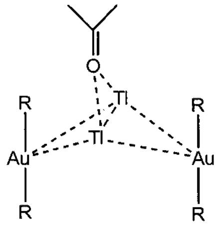

Figure 4. Butterfly tetranuclear structure; R = C_6Cl_5

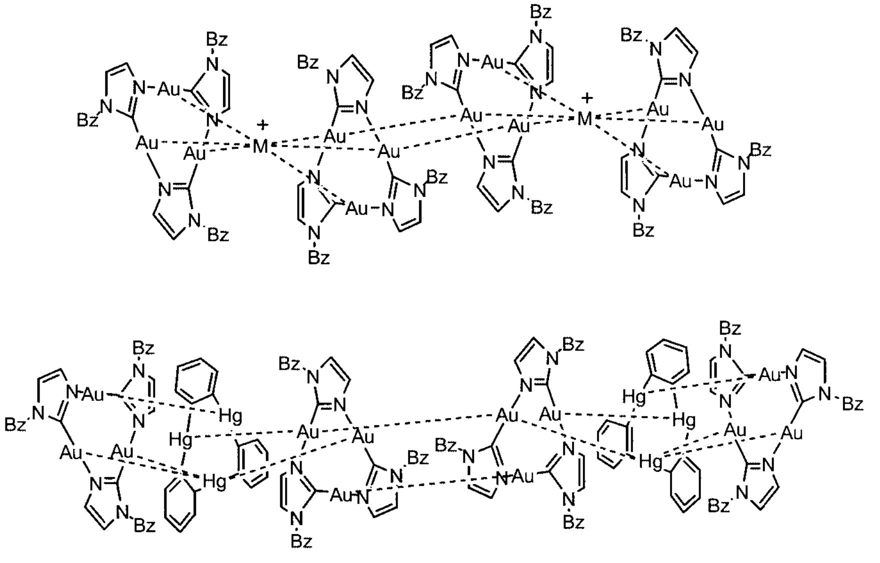

Figure 5. Sandwich heterometalllic clusters; top: silver(I)− or thallium(I)−gold(I) (M = Ag, Tl); bottom: mercury(II)−gold(I)

2.2. By Use of Trinuclear Cyclic Gold(I) Derivatives as Bases

Burini et al. have recently described[40−42] a series of sandwich derivatives obtained through the interaction between π-base trinuclear gold(I) complexes, such as $[Au(\mu\text{-}N^3,C^2\text{-bzim})]_3$ (N^3,C^2-bzim = 1-benzylimidazolate) and $[Au(\mu\text{-}C(OMe){=}NCH_3)]_3$, and either acid cations such as Ag^+ or Tl^+, or the π molecular acid trinuclear complex of mercury(II) $[Hg(\mu\text{-}C,C\text{-}C_6F_4)]_3$, giving $[M\{[Au(\mu\text{-}N^3,C^2\text{-bzim})]_3\}_2]^+$ (M= Ag, Tl), $[Tl\{[Au(\mu\text{-}C(OMe){=}NCH_3)]_3\}_2]PF_6$, $\{[Au(\mu\text{-}N^3,C^2\text{-bzim})]_3\}_2[Hg(C_6F_4)]_3$ or $\{[Au(\mu\text{-}C(OMe){=}NCH_3)]_3\}_2[Hg(C_6F_4)]_3$, containing $[Au_3MAu_3]$ (M = Ag^I, Tl^I) or $[Au_3Hg_3Au_3]$ units (Figure 5). Additional gold−gold contacts therefore produce a supramolecular chain.

The naked silver or thallium ion center is bonded to six gold atoms to form a distorted trigonal prism, with gold−silver distances from 2.731(2) to 2.922(2) Å and gold−thallium distances from 2.9711(7) to 3.1075(4) Å. In addition to this, there are also gold−gold interactions in the cyclic trimer moiety (an average of 3.19 Å in the mixed gold−silver cluster, for instance) and between two close sandwich units [3.116 and 3.268 Å for the gold−silver cluster, or from 3.0588(4) to 3.1089(7) Å in the gold−thallium clusters].

The mercury centers interact with the gold centers in adjacent rings, with gold−mercury distances as short as 3.27 and 3.24 Å, for bzim and $C(OMe){=}NCH_3$ ligands, respectively. DFT calculations showed positive electrostatic potential values above and below the plane of the mercury ring, while similar regions for the gold ring had negative values, thus clearly demonstrating the electrostatic nature of the interaction between the electron-poor mercury and the electron-rich gold rings.

The emission spectra of these compounds (silver and thallium) display low-energy phosphorescence, consistent with the extended chain structure. Furthermore, they exhibit luminescence thermochromism with red shifts in their emission maxima when they are cooled from room temperature to 77 K. The gold−mercury derivatives luminesce both at ambient and at low temperatures, the intensity of the emission increasing upon gold−mercury interaction.

2.3. By Encapsulation of a Metal Center by a Dinuclear Gold(I) Cryptand

Catalano and co-workers have recently developed an interesting approach to this subject. They have prepared metallocryptands with a cavity in which metallic centers can be encapsulated by use of metal−metal closed-shell interactions. Firstly, they synthesized a dinuclear gold(I) cryptand, employing the ligand 2,9-bis(diphenylphosphanyl)-1,10-phenantroline (P_2phen), which is able to selectively host Tl^I, Na^I (weakly; dissociates readily as there are no important closed-shell interactions), or Hg^0 (Figure 6).[43,44] Complexes $[Au_2M(P_2phen)_3](PF_6)_3$ (M = Tl, Hg) each display an almost linear arrangement with very short gold−thallium distances [2.9109(5) and 2.9171(5) Å] or gold−mercury distances [2.7807(4) and 2.7847(4) Å]. The structures contain two trigonal Au^I centers capping a D_3 symmetric cage. The gold−thallium derivative is strongly luminescent at 600 nm, both in solution and in the solid state; the emission can be attributed to metal-centered phosphorescence based on its large Stoke's shift, long lifetime, and solvent independence. The gold−mercury derivative is weakly emissive at 580 nm.

These workers have also extended the system to d^{10} Pd^0- and Pt^0-based metallocryptates [rather than gold(I)] capable of hosting a Tl^I or a Pb^{II} center through $d^{10}{-}s^2$ closed-shell interactions.[45−47] They have also changed the P_2phen ligand for other ligands such as 2,9-bis(diphenylphosphanyl)-1,8-naphthyridine (dppn) or PPh_2py; gold(I) centers have also been exchanged for silver(I). X-ray studies of $[Au_2$-

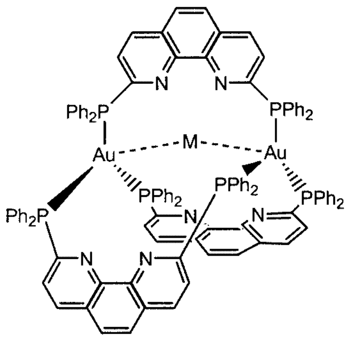

Figure 6. Metallocryptates $[Au_2M(P_2phen)_3](PF_6)_3$

$Na(dppn)_3](PF_6)_3$ display long gold−sodium interactions around 3.5 Å.[48] Moreover, these workers have also prepared a series of alkaline encapsulated derivatives $[Au_2M(dppn)_3](PF_6)_3$ (M = Li, Na, K, Cs), which also display luminescence around 580 nm in the solid state; the emission has been assigned to a gold-centered phosphorescence due to the tricoordinate gold centers.

2.4. Other Cases

Haupt and co-workers have prepared the trimetallic tetrahedron complexes $[Re_2(AuPPh_3)(MPPh_3)(\mu\text{-}PCy_2)(CO)_7(-)$-thiocamphanate] (M = Cu, Ag), which show the short metal−metal distances of 2.584(2) Å (copper−gold) and 2.7026(18) Å (gold−silver).[49] The rhenium core is supported by phosphido ligands, but the gold−silver or gold−copper bond is unsupported. Moreover, the copper or silver center is coordinated to the sulfur atoms of the thiocamphanate ligand.

M. Laguna and co-workers have crystallographically characterized the pentanuclear derivative $[Au_4Ag(CH_2SiMe_3)_4(\mu\text{-}dppm)_2]CF_3SO_3$ (dppm = $PPh_2CH_2PPh_2$) (Figure 7)[50] with an Au_4Ag core, which displays a silver atom bonded solely to four gold atoms in a distorted tetrahedral environment. The four silver−gold distances lie between the values of 2.7179(13) and 2.7822(13) Å and are almost identical to those found for our unsupported silver(I)−gold(I) bonds. Similarly, the gold−gold distances are 3.2170(9) and 3.2773(12) Å.

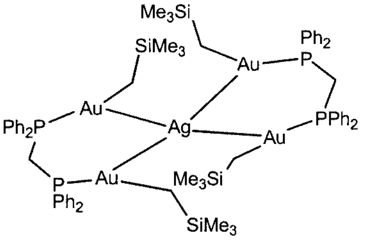

Figure 7. Pentanuclear Au_4Ag derivative with a tetrahedral geometry

The same workers have also synthesized the heptanuclear cluster $[Au_6Ag\{\mu\text{-}C_6H_2(CHMe_2)_3\}_6]CF_3SO_3$ with an almost planar Au_6Ag core, resembling a "cartwheel", in which the silver(I) atom is at the center of a regular hexagon of gold atoms (Figure 8).[51] The gold−silver distances are quite short − 2.797(1), 2.802(1), and 2.809(1) Å − whilst the gold−gold distances range from 2.795(1) to 2.817(1) Å, slightly longer than in the homoleptic pentamer $[\{Au(mes)\}_5]$ [2.692(1), 2.697(1) and 2.708(2) Å; mes = 2,4,6-$Me_3C_6H_2$].[52] The tris(isopropylphenyl) groups serve as bridges between two consecutive gold atoms within the hexagon. The derivative shows a deep green color, but it is not luminescent.

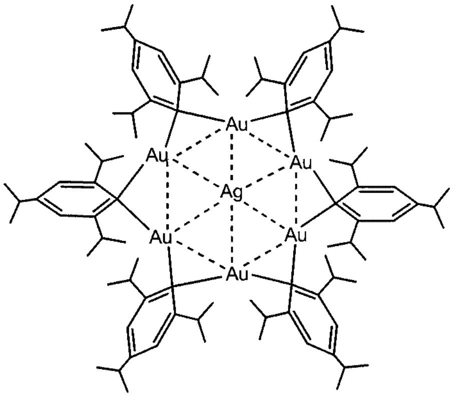

Figure 8. Heptanuclear Au_6Ag derivative with hexagonal geometry

Table 1 summarizes the gold−silver distances for this type of derivatives, their main characteristic being that all of them are quite short, often with additional gold−gold interactions. Table 2 summarizes the gold−thallium distances for unsupported bonds, which are also very short, although the presence of gold−gold interactions is less common.

3. Derivatives with Supported Gold-Metal Bonds

The use of bridging ligands favors the proximity of metal centers and therefore the presence of short distances. Moreover, these short distances are easily preserved in solution, thanks to the bridge. As is the case of unsupported gold(I)−metal bonds, the conformations of the ligands, the aggregation of the molecules, and the optical properties can be dramatically changed by the presence of these gold−metal closed-shell interactions. Very common is the use of C-donor bridging ligands that are good σ-donor ligands. These form deficient bonds and induce very short metal−metal distances. Nevertheless, ambidentate bridging ligands favor heteronuclear complexes.

3.1. Dinuclear Derivatives

For dinuclear derivatives, the simplest case, no example of copper−gold is yet known, but four gold−silver compounds have recently been crystallographically characterized. The first, reported by Schmidbaur and co-workers,[53] is $[AuAg(PPh_2py)_2](ClO_4)_2$, with a gold−silver distance of 2.820(1) Å. Two more examples − [Au-

Table 1. $Ag^{I}-Au^{I}$ distances [Å] reported in derivatives with unsupported gold−silver interactions

Compound	$Ag^{I}-Au^{I}$	Au−Au	Ag−Ag	Ref.
$[(C_6F_5)_2Au(\mu\text{-}AgSC_4H_8)_2Au(C_6F_5)_2]_\infty$	2.718(2), 2.726(2)	yes	no	[30]
$[(C_6F_5)_2Au(\mu\text{-}AgC_6H_6)_2Au(C_6F_5)_2]_\infty$	2.702(2), 2.792(2)	yes	no	[31]
$[(Ph_3PCH_2)_2Au(\mu\text{-}AgPPh_3)_2Au(CH_2PPh_3)_2]$	2.760(2), 2.783(2)	no	no	[32]
$[(C_6F_5)_2Au(\mu\text{-}AgOCMe_2)_2Au(C_6F_5)_2]_\infty$	2.7829(9), 2.7903(9)	yes	yes	[33]
$[Ag\{[Au(\mu\text{-}N^3,C^2\text{-bzim})]_3\}_2]BF_4$	2.731(2)−2.922(2)	yes	no	[41]
$[Au_4Ag(CH_2SiMe_3)_4(\mu\text{-dppm})_2]CF_3SO_3$	2.7179(13), 2.7822(13)	yes	no	[50]
$[Au_6Ag\{\mu\text{-}C_6H_2(CHMe_2)_3\}_6]CF_3SO_3$	2.797(1),2.802(1), 2.809(1)	yes	no	[51]
$[Re_2(AuPPh_3)(AgPPh_3)(\mu\text{-}PCy_2)(CO)_7(-)\text{-thiocamphanate}]$	2.7026(18)	no	no	[49]

Table 2. $Au^{I}-Tl^{I}$ distances [Å] reported in derivatives with unsupported gold−thallium interactions

Compound	$Au^{I}-Tl^{I}$	Au−Au	Tl−Tl	Ref.
$[Tl(OPPh_3)_2][Au(C_6F_5)_2]$	3.0358(8), 3.0862(8)	no	no	[35]
$[Tl(OPPh_3)][Tl(OPPh_3)(THF)][Au(C_6Cl_5)_2]_2$	3.0529(3)−3.3205(3)	no	no	[36]
$[Tl(OPPh_3)][Tl(OPPh_3)(acetone)][Au(C_6Cl_5)_2]_2$	3.0937(3)−3.2705(4)	no	no	[36]
$[Tl(bipy)]_2[Au(C_6F_5)_2]_2$	3.0161(2)	yes	no	[37]
$[Tl(bipy)][Tl(bipy)_{0.5}(THF)][Au(C_6Cl_5)_2]_2$	3.0323(4), 3.0540	no	no	[37]
$[Au_2Tl_2(C_6Cl_5)_4]OCMe_2$	3.0331(6)−3.1887(6)	no	yes	[39]
$[Tl\{[Au(\mu\text{-}N^3,C^2\text{-bzim})]_3\}_2]BF_4$	2.9711(7)−3.0448(7)	yes	no	[41]
$[Tl\{[Au(\mu\text{-}C(OMe){=}NCH_3)]_3\}_2]PF_6$	3.0673(4)−3.1075(4)	yes	no	[41]
$[Au_2Tl(P_2phen)_3](PF_6)_3$	2.9109(5), 2.9171(5)	no	no	[43]

$Ag(PPh_2CH_2SPh)_2](CF_3SO_3)_2$ and $[AuAg(PNH_2)_2](CF_3SO_3)_2$ [PNH_2 = 2-(diphenylphosphanyl)aniline] − with longer gold−silver distances [2.9314(5) and 2.9931(12) Å, respectively] have been prepared by us.[54,55] Finally, Fackler and co-workers have prepared $[AgAu(\mu\text{-}CH_2P(S)Ph_2]_2$, with a gold−silver distance of 2.9124(13) Å and an intermolecular gold−silver distance of 3.635 Å, forming a chain structure (Figure 9, b).[56] The same strategy − use of a bridging ambidentate ligand capable of selectively coordinating to the gold(I) center through a P- or C-donor atom, whilst the silver(I) center is coordinated to the second donor atom (N or S) − was used in all four cases. According to ab initio calculations carried out on a model based in the derivative $\{[AuM(PH_2CH_2SH)_2]^{2+}$; M= Cu, Ag, Au}, the presence of only one gold atom is sufficient to induce metallophilic attractions in copper and silver, and this effect can be modulated depending on the gold ligand. It has also been shown theoretically that the isomer found (phosphorus−gold-bonded system) is not only the most stable, but it also produces the shortest gold−silver distance (3.060 Å).

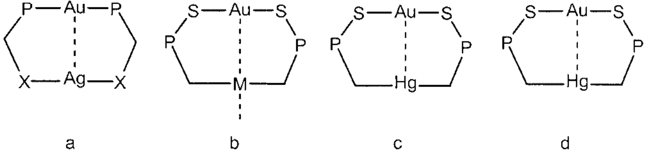

Figure 9. Doubly bridged dinuclear gold−silver(I), −mercury(II), or −thallium(I) derivatives: a) P−C−X = PPh_2py, PPh_2CH_2SPh, 2-(diphenylphosphanyl)aniline; b), c), d) M = Ag, Tl; C−P−S = $CH_2P(S)Ph_2$

Fackler and co-workers have prepared a dinuclear derivative, $[AuHg\{\mu\text{-}CH_2P(S)Ph_2\}_2]PF_6$, which displays a short gold(I)−mercury(II) distance of 3.088(1) Å (Figure 9, c).[57] It is a doubly bridged complex with the mercury centers coordinated to the ylide carbon atom and the gold centers coordinated to the sulfur atom (mercury and gold are not easy distinguished by X-ray diffraction studies, but NMR could determine the isomer: one kind of methylene signals with mercury satellites). A second X-ray structure was found for this derivative: it has a dimeric structure with gold−mercury distances of 2.9891(9) Å and a gold−gold intermolecular distance of 3.150(2) Å. These workers have also prepared the same derivative but with $[AuCl_4]$ as anion; in this case the gold(I)−mercury distance is 3.079 (2) Å and there is a gold(I)−gold(III) distance of 3.402(2) Å.[58]

Similarly, they have also prepared the dinuclear derivative $[AuTl\{\mu\text{-}CH_2P(S)Ph_2\}_2]_\infty$, a doubly bridged complex with the thallium centers coordinated to the ylide carbon atom and the gold centers coordinated to the sulfur atom. This also displays a short gold(I)−thallium(I) distance of 2.959(2) Å (Figure 9, d), but it forms an extended one-dimensional linear-chain polymer with an additional gold−thallium distance of 3.003(2) Å. This derivative is strongly photoluminescent, emitting at 575 nm (solid state 298 K) with a lifetime of 0.98 µs; the long lifetime and large separation between excitation and emission peaks indicate that the emission process is phosphorescence. This optical property has been related to the gold−thallium bonds by calculation by the Fenske−Hall method.[59,60]

3.2. Trinuclear Derivatives

There are no trinuclear copper−gold clusters in which the presence of short metal−metal distances has been reported. For gold−silver derivatives there are three examples, two of them using a C-donor bridging ligand and one with a diphosphane ligand.

Vicente and co-workers have structurally characterized the trinuclear derivative $[(AuPPh_3)_2\{\mu\text{-}[C(PPh_3)(C_5H_4N\text{-}2)]\}\{\mu\text{-}Ag(O_2NO)(OClO_3)\}]$, with a triangular geometry for the metallic centers (Figure 10) and the presence of supported gold−gold [3.078(1) Å] and gold−silver interactions [2.926(1) and 3.006(1) Å].[61,62] In that work, in order to distinguish clusters with weak interactions from conventional clusters in which some or all metal atoms are tightly bonded, the former were denoted as "loose" clusters. This nomenclature has been adopted by other authors.

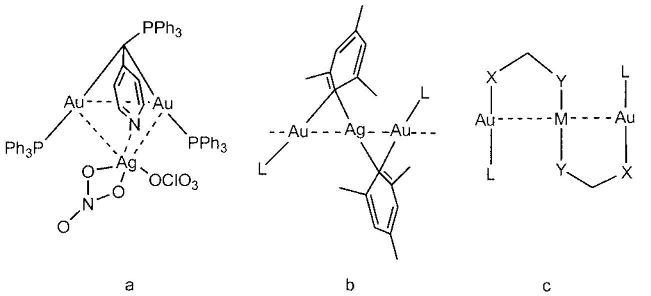

Figure 10. Molecular structures found for trinuclear Au_2Ag compounds: a) $[(AuPPh_3)_2\{\mu\text{-}[C(PPh_3)(C_5H_4N\text{-}2)]\}\{\mu\text{-}Ag(O_2NO)(OClO_3)\}]$, b) $[\{LAu(\mu\text{-mes})\}_2Ag](ClO_4)$, L = $AsPh_3$, c) M = Ag, L = mes, X−C−Y = dppm; M = Hg, L = Cl, X−C−Y = $CH_2P(S)Ph_2$

The mesityl group ($2,4,6\text{-}Me_3C_6H_2$) acts as a bridge, through three-center, two-electron bonds, and it is able to induce very short metal−metal distances, as, for instance, in the homoleptic derivatives $[\{Au(mes)\}_5]$ [2.692(1), 2.697(1) and 2.708(2) Å] and $[\{Ag(mes)\}_4]$ [2.733(3) and 2.7553(3) Å].[52] We have used this ligand to prepare heteronuclear gold−silver compounds containing trinuclear moieties $[\{(AsPh_3)Au(\mu\text{-mes})\}_2Ag](ClO_4)$ with a linear arrangement of the metallic core and a short gold−silver distance of 2.7758(8) Å; these trinuclear units are connected by gold−gold contacts of 3.132(2) Å to form a chain polymer.[63] By a similar approach, we have also prepared a diphosphane-bridged trinuclear derivative $[\{(mes)Au(\mu\text{-}dppm)\}_2Ag](ClO_4)$ with longer gold−silver distances [2.944(2) and 2.946(2) Å] due to the bridging ligand (Figure 10).[64]

Fackler and co-workers have prepared the trinuclear derivative $[Au_2Hg\{\mu\text{-}CH_2P(S)Ph_2\}_2Cl_2]$, which displays a linear arrangement with a central mercury atom and gold−mercury distances of 3.310(1) and 3.361(1) Å (Figure 10). As found in the dinuclear gold−mercury derivative, the mercury center is coordinated to the ylide carbon atom and the gold centers coordinated to the sulfur atom.[58]

3.3. Higher Nuclearities

Abu-Salah et al. reported the tetranuclear cluster $[(PPh_3)Ag\{\mu\text{-}Au(CCPh)_2\}_2Ag(PPh_3)]$, with the same metallic core as in the derivatives described above (Ag_2Au_2 in section 2.1.1., Figure 1), except for a change in the positions of gold and silver (Figure 11).[65] Moreover, the main structural differences are as follows: silver centers do not aggregate (or show a lesser tendency than gold in the presence of a bulky phosphane) and so no polymer is formed; the alkyne fragments are coordinated to the silver centers, thus acting as bridging ligands. The gold−silver distances range from 2.894(1) to 3.028(1) Å, indicating appreciable metal−metal bonding; there are no gold−gold contacts (4.013 Å).

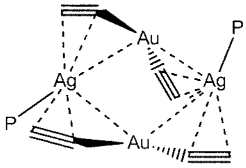

Figure 11. Rhomboidal, nearly square-planar geometry with supported gold−silver bonds; P = PPh_3

Pentanuclear clusters $[Au_3M_2(\mu\text{-}CCPh)_6]^-$ (M = Cu, Ag) displaying a trigonal-bipyramidal arrangement for the metallic core with the copper or silver centers in the apical positions have also been reported.[66−68] The gold−copper distances range from 2.783(3) to 3.016(3) Å [from 2.800 to 3.115(3) Å in a second X-ray diffraction study] whilst the gold−silver distances range from 2.911(1) to 3.096(1) Å [from 2.877(1) to 2.998(1) Å in a second X-ray determination]; there are no gold−gold contacts. Each gold center is coordinated to two alkynyl ligands, whilst the copper or silver centers are coordinated to the alkyne groups and to the gold atoms.

Eisenberg and co-workers have reported the tetranuclear heterodimetallic derivative $[\{AuCu(\mu\text{-}SPy)(\mu\text{-}PPh_2py)\}_2](PF_6)_2$, which is composed of two $AuCu(\mu\text{-}SPy)(\mu\text{-}PPh_2py)$ units (Cu bonded through N- and Au through P- and S-donor atoms) held together by bridging thiolate ligands (Figure 12).[69] There are strong gold−copper interactions of 2.6339(7) and 2.6455(7) Å in each dinuclear unit. This derivative is strongly emissive in the solid state at 77 K and in solution, whilst the mononuclear starting derivative $[Au(SPy)(PPh_2py)]$ shows weaker photoluminescence. The emitting state has been tentatively assigned to LMCT transition (from S to Au), but it has been strongly modified by the coordination of Cu to S and the formation of gold−copper bonds.

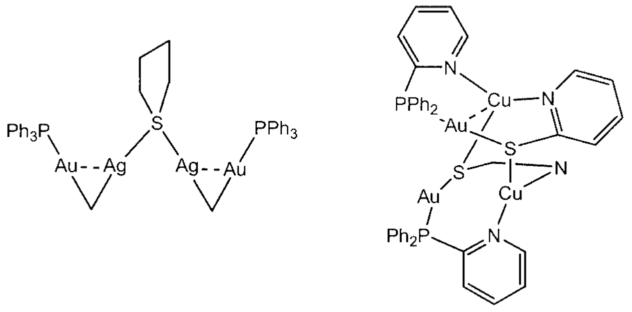

Figure 12. Two dimers bridged by ligands

We have also used the mesityl ligand to prepare heteronuclear gold−silver derivatives, such as [(PPh$_3$)Au(μ-mes){Ag(μ-SC$_4$H$_8$)}$_2$(μ-mes)Au(PPh$_3$)], which has a gold−silver distance of 2.8245(6) Å, quite short but longer than the first unsupported bonds.[70] The structure possesses a dinuclear gold−silver core, which is bonded to an equal second unit through two tetrahydrothiophene bridges (Figure 12).

We have prepared the tetranuclear mixed derivative [Au$_2$Ag$_2$(C$_6$F$_5$)$_2$(PPh$_2$CH$_2$SPh)$_2$(CF$_3$CO$_2$)$_2$] by treating the mononuclear *P*-bonded derivative [Au(C$_6$F$_5$)(PPh$_2$CH$_2$SPh)] with AgCF$_3$CO$_2$.[54] The silver(I) centers are coordinated to the sulfur atom and bridged to each other by the trifluoroacetate ligands. There are two short gold−silver distances of 3.0335(8) Å and one short silver−silver distance of 2.8155(9) Å, so its geometry is a zigzag chain (Figure 13).

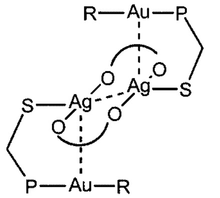

Figure 13. Tetranuclear derivative with a zigzag chain; O−O = CF$_3$CO$_2$, R = C$_6$F$_5$, P−C−S = PPh$_2$CH$_2$SPh

Henkel and co-workers have characterized the heterodimetallic clusters [Au$_3$Cu$_3$L$_4$]$^{2-}$ and [Au$_2$Ag$_4$L$_4$]$^{2-}$ (L = ethane-1,2-dithiolate), each of which displays a typical M$_6$S$_8$ cage skeleton with two gold atoms in the apical position, as shown in Figure 14.[71] The copper derivative shows short copper−gold distances of 2.862 Å on average, whilst the silver derivative displays gold−silver distances of 2.996 Å on average and silver−silver distances of 3.170 Å on average.

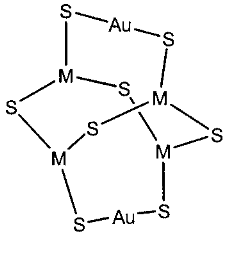

Figure 14. M$_6$S$_8$ cage skeleton

Salter et al. have reported the X-ray structures of heterotrimetallic hexanuclear clusters [AuCuRu$_4$(μ$_3$-H)$_2$(μ-dppf)(CO)$_{12}$] [dppf = 1,1′-bis(diphenylphosphanyl)ferrocene] and [AuCuRu$_4$(μ$_3$-H)$_2$(μ-dppe)(CO)$_{12}$] (dppe = PPh$_2$CH$_2$CH$_2$PPh$_2$), obtained through metal exchange reactions.[72,73] The metal-framework structures of both can be described as intermediate between a capped trigonal bipyramid and a capped square pyramid (Figure 15). There are short copper− and gold−ruthenium distances and also short copper−gold distances of 2.641(1) and 2.614(2) Å, respectively, for dppf and dppe. Moreover, the diphosphane ligand is bridging the copper and gold centers.

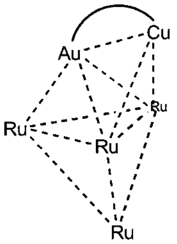

Figure 15. AuCuRu$_4$ cluster core in which a diphosphane ligand is bridging the copper and gold centers

We summarize silver(I)− and copper(I)−gold(I) distances found in mixed derivatives with supported bonds in Tables 3 and 4, respectively. Table 5 summarizes thallium−(supported bonds) and mercury−gold distances.

Finally, we describe two cases not exactly within the scope of this microreview, the first for copper(I)−gold(III) bonds, the second for gold−indium bonds. In the first case, Coucouvanis and co-workers have reported that the X-ray structure of [AuCu$_4$L$_4$]$^-$ [L = 2,2-bis(*tert*-butoxycarbonyl)-1-thiolatoethene-1-perthiolate consists of a rectangular pyramidal AuCu$_4$ core with mean Au^{III}−Cu^{I} bonds of 3.029(7) Å.[74]

Now, to date there are only two clusters showing short gold−indium distances, and although the oxidation state of the starting materials is +1 for both metals, their final oxidation states are unclear. Schmidbaur and co-workers have reported the hexanuclear clusters [Au$_3$In$_3$Cl$_6$(THF)$_6$(dppe)$_2$] and [Au$_3$In$_3$Br$_7$(THF)$_6$(dppe)$_2$]$^-$, obtained by the insertion of InX into the Au−X bond of [AuXPPh$_3$].[75,76] The metallic core is formed by an isosceles triangle of three gold atoms, two indium atoms capping the gold triangle on both faces, while the third indium atom bridges the shortest edge of the gold triangle. Thus, there are two short gold−gold distances of 2.931(1) and 2.939(1) Å (for Cl), 2.860(1) and 2.858(1) Å (for Br), and one very short gold−gold distance of 2.562(1) Å and 2.571(1) Å, respectively, for Cl and Br. The gold−indium distances range from 2.761(1) to 2.973(1) Å (for Br). Theoretical investigations proposed two gold(0) and one gold(I)

Table 3. Ag^I-Au^I distances [Å] reported in derivatives with supported gold−silver interactions

Compound	Ag^I-Au^I	Ref.
$[AuAg(PPh_2py)_2](ClO_4)_2$	2.820(1)	[53]
$[AuAg(PPh_2CH_2SPh)_2](CF_3SO_3)_2$	2.9314(5)	[54]
$[AuAg(PNH_2)_2](CF_3SO_3)_2$	2.9931(12)	[55]
$[AgAu(\mu\text{-}CH_2P(S)Ph_2]_2]$	2.9124(13)	[56]
$[(AuPPh_3)_2\{\mu\text{-}\{C\text{-}(PPh_3)(C_5H_4N\text{-}2)\}\}\{\mu\text{-}Ag(O_2NO)(OClO_3)]$	2.926(1), 3.006(1)	[61]
$[\{(AsPh_3)Au(\mu\text{-}mes)\}_2Ag](ClO_4)$	2.7758(8)	[63]
$[\{(mes)Au(\mu\text{-}dppm)\}_2Ag](ClO_4)$	2.944(2), 2.946(2)	[64]
$[(PPh_3)Ag\{\mu\text{-}Au(CCPh)_2\}_2Ag(PPh_3)]$	2.894(1)−3.028(1)	[65]
$[(PPh_3)Au(\mu\text{-}mes)\{Ag(\mu\text{-}SC_4H_8)\}_2(\mu\text{-}mes)Au(PPh_3)]$	2.8245(6)	[70]
$[Au_2Ag_2(C_6F_5)_2(PPh_2CH_2SPh)_2(CF_3CO_2)_2]$	3.0335(8)	[54]
$[Au_3Ag_2(\mu\text{-}CCPh)_6]^-$	2.911(1)−3.096(1), 2.877(1)−2.998(1)	[67,68]
$[Au_2Ag_4L_4]^{2-}$ (L = ethane-1,2-dithiolate)	average 2.996 Å	[71]

Table 4. Au^I-Cu^I distances [Å] found in derivatives with gold−copper interactions

Compound	Au^I-Cu^I	Ref.
$[Re_2(AuPPh_3)(CuPPh_3)(\mu\text{-}PCy_2)(CO)_7\{(-)\text{-thiocamphanate}\}]$	2.584(2)	[49]
$[\{AuCu(\mu\text{-}Spy)(\mu\text{-}PPh_2py)\}_2](PF_6)_2$	2.6339(7), 2.6455(7)	[69]
$[Au_3Cu_2(\mu\text{-}CCPh)_6]^-$	2.783(3)−3.016(3), 2.800−3.115(3)	[66,67]
$[Au_3Cu_3L_4]^{2-}$ (L = ethane-1,2-dithiolate)	average 2.862	[71]
$[AuCuRu_4(\mu_3\text{-}H)_2(\mu\text{-}dppf)(CO)_{12}]$	2.641(1)	[72]
$[AuCuRu_4(\mu_3\text{-}H)_2(\mu\text{-}dppe)(CO)_{12}]$	2.614(2)	[73]

Table 5. Thallium(I)−, mercury(0)−, and mercury(II)−gold(I) distances [Å] found in derivatives with gold−metal interactions

Compound	Au^I-M	Ref.
$[AuTl(\mu\text{-}CH_2P(S)Ph_2]_2]_\infty$	2.959(2)	[59]
$[AuHg(\mu\text{-}CH_2P(S)Ph_2]_2]PF_6$	3.088(1)	[57]
$[AuHg(\mu\text{-}CH_2P(S)Ph_2]_2]PF_6$	2.9891(9)	[57]
$[AuHg(\mu\text{-}CH_2P(S)Ph_2]_2][AuCl_4]$	3.079(2)	[58]
$[Au_2Hg(\mu\text{-}CH_2P(S)Ph_2]_2Cl_2]$	3.310(1), 3.361(1)	[58]
$\{[Au(\mu\text{-}N^3,C^2\text{-}bzim)]_3\}_2[Hg(C_6F_4)]_3$	3.27	[42]
$\{[Au(\mu\text{-}C(OMe){=}NCH_3)]_3\}_2[Hg(C_6F_4)]_3$	3.24	[42]
$[Au_2Hg(P_2phen)_3](PF_6)_2$	2.7807(4), 2.7847(4)	[44]

centers, so it is not appropriate to view them as closed-shell interactions.

Acknowledgments

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