



Theoretical study of the closed-shell d^{10} – d^{10} Au(I)–Cu(I) attraction in complexes in extended unsupported chains

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ABSTRACT

Model compounds are used to study the metallophilic attraction between gold and copper atoms. Ab initio calculations on dimers and tetramers in different distributions of the simplified units are analyzed. An attraction is found for all models and there is a reasonable agreement between the experimental and theoretical geometries.

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1. Introduction

In the last two decades the bonding interaction between gold(I) and closed-shell (d^8 – d^{10} – s^2) systems has been widely studied from the experimental and theoretical viewpoints [1–3]. Non-covalent interactions range from extremely weak van der Waals forces, as for example in the helium dimer, with interaction energies of 0.091 kJ/mol, to metallophilic (of approximately 25 kJ/mol) and extremely strong interactions [4–6]. In fact, it is possible to find reports in the literature for diatomic systems with strong closed-shell d^{10} – s^2 interactions such as AuHg⁺ and AuXe⁺ with interaction energies of 179 and 87 kJ/mol, respectively [7,8]. In these systems, two complementary forces have been identified: charge-induced dipole and dispersion interactions [6,9].

Gold(I)-containing heterometallic systems in which short closed-shell metal–metal interactions are present (metallophilicity) can also be found in the literature [10,11]. We have used basic aurates such as $[\text{AuR}_2]^-$ ($\text{R} = -\text{C}_6\text{F}_5$, $-\text{C}_6\text{F}_3\text{Cl}_2$ and $-\text{C}_6\text{Cl}_5$) to react with Lewis acid metal salts, what allows us to isolate complexes bearing unsupported Au(I)–M interactions ($\text{M} = \text{Ag(I)}$ [12,13], Cu(I) [14,15], Tl(I) [16,17], and Bi(III) [18]). From ab initio studies, metallophilic interactions have been described using correlated methods. It has been shown that metallophilic interactions arise

from dispersion-type correlation effects (van der Waals) and charge transfer contributions [17,19].

The formation of Au–M interactions based on acid–base reactions like, for instance, those between Tl^+ or Ag^+ (Lewis acids) and $[\text{AuR}_2]^-$ ($\text{R} = \text{C}_6\text{F}_5$ or C_6Cl_5) (Lewis bases), provides an additional electrostatic attraction [20]. We have succeeded in synthesizing Au–Tl complexes by reacting a $[\text{AuR}_2]^-$ Lewis base with a Tl^+ salts, which acts as Lewis acids [21,22]. From a theoretical point of view, the metallophilicity between gold(I) and thallium(I) centers in these compounds gives an average metal–metal separation of 300 pm and the interaction energy is estimated to be about 276 kJ/mol, of which 80% has an ionic origin [17].

In the particular case of the complex $[\text{Tl}(\text{bipy})_2][\text{Au}(\text{C}_6\text{F}_5)_2]$ [20] in the solid state, its solid state structure consists of a planar polymeric arrangement formed by the repetition of Tl–Au–Au–Tl units in which the fragment charges follow the pattern $[+---+]$. We found that the intermetallic are due to electronic correlation and ionic effects [19]. Both effects are important when we consider the training of the polymer from smaller units. The most stable energy is found for the $[+---+]$ pattern, in accordance with the experimentally observed arrangement.

In view of our previous experimental and theoretical results, we have focused our attention on Cu(I) as heterometal. We have reported the first unsupported Au(I)–Cu(I) interactions among the metallic fragments present in $[\text{Au}(\text{C}_6\text{F}_5)][\text{Cu}(\text{NCCH}_3)-\mu_2-\text{C}_4\text{H}_4\text{N}_2]_n$, $[\text{Au}(\text{C}_6\text{F}_5)_2][\text{Cu}(\text{NCCH}_3)_2]$, $[\text{Au}(\text{C}_6\text{F}_5)_2][\text{Cu}(\text{NCCH}_3)_2]$ and $[\text{Au}(\text{C}_6\text{F}_5)_2][\text{Cu}(\text{NPh})_2]$ [14,15]. These complexes show

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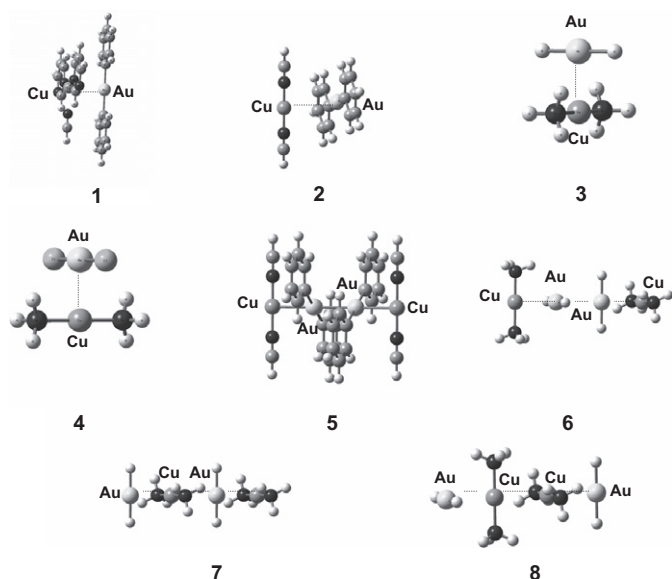


Fig. 1. Theoretical model systems.

unsupported Au(I)··Cu(I) metallophilic interactions and interesting photophysical properties. The solid state crystal structure of the complex $[\text{Au}(\text{C}_6\text{F}_5)_2]_2[\text{Cu}(\text{NCPH})_2]_2$ consists of a tetramer formed by two gold fragments and two copper fragments joined together through unsupported Au··Cu and Au··Au contacts, leading to a Cu–Au–Au–Cu arrangement, analogous to that in complex $[\text{Ti}(\text{bipy})_2][\text{Au}(\text{C}_6\text{F}_5)_2]$ see above.

In this paper we report ab initio calculations at Hartree–Fock (HF) and Møller–Plesset (MP2) levels of theory on simplified model systems using quasi-relativistic effective core potentials in order to study the nature of the d^{10} – d^{10} Au(I)··Cu(I) interaction for di- and tetranuclear species. This allowed us to understand the forces that operate in building up the supramolecular arrangements in the solid state.

2. Models and computational details

The crystal structures of the compounds $[\text{Au}(\text{C}_6\text{F}_5)][\text{Cu}(\text{NCCH}_3)(\mu_2\text{-C}_4\text{H}_4\text{N}_2)]_n$, $[\text{Au}(\text{C}_6\text{F}_5)]_2[\text{Cu}(\text{NCCH}_3)_2]$, $[\text{Au}(\text{C}_6\text{F}_5)]_2[\text{Cu}(\text{NCCHCHPh})_2]$ and $[\text{Au}(\text{C}_6\text{F}_5)]_2[\text{Cu}(\text{NCPH})_2]_2$ [14,15] were used

Table 1
Experimental values for the metallophilic attraction from crystal-structures.

System	Au–Cu/pm	Au–Au/pm
$[\text{Au}(\text{C}_6\text{F}_5)]_2[\text{Cu}(\text{NCCH}_3)_2]$ [14]	293.4	
$[\text{Au}(\text{C}_6\text{F}_5)]_2[\text{Cu}(\text{NCPH})_2]$ [14]	267.3	
$[\text{Au}(\text{C}_6\text{F}_5)]_2[\text{Cu}(\text{NCCH}=\text{CHPh})_2]_2$ [14]	261.6	300.1
	260.9	
$[\text{Au}(\text{C}_6\text{F}_5)]_2[\text{Cu}(\text{NCCH}_3)(\mu_2\text{-C}_4\text{H}_4\text{N}_2)]_n$ [15]	282.2	

to build theoretical models, which are depicted in Fig. 1. The original F–, –NCCH₃, –NCPH and $\mu_2\text{-C}_4\text{H}_4\text{N}_2$ ligands were replaced by H–, Cl–, –NCH and C₅H₅N–. In the present work the simplified models were used to study the d^{10} – d^{10} intermolecular interaction between Cu(I) and Au(I) centers. Also, in order to estimate the d^{10} – d^{10} intermolecular interaction and the charge on each monomer, we included reduced models of dimers and tetramers with the general formula: $[\text{Au}(\text{C}_6\text{H}_5)_2]_2 \cdots [\text{Cu}(\text{py})_2(\text{NCH})]$ (**1**), $[\text{Au}(\text{C}_6\text{H}_5)_2]_2 \cdots [\text{Cu}(\text{NCH})_2]$ (**2**); $[\text{AuX}_2][\text{Cu}(\text{NH}_3)_2]$ (**3,4**) X = H,Cl; $[\text{Cu}(\text{NCH})_2][\text{Au}(\text{C}_6\text{H}_5)_2] \cdots [\text{Cu}(\text{NCH})_2][\text{Au}(\text{C}_6\text{H}_5)_2]$ (**5**); $[\text{Cu}(\text{NH}_3)_2][\text{AuH}_2] \cdots [\text{AuH}_2][\text{Cu}(\text{NH}_3)_2]$ (**6**); $[\text{Cu}(\text{NH}_3)_2][\text{AuH}_2] \cdots [\text{Cu}(\text{NH}_3)_2][\text{AuH}_2]$ (**7**) and $[\text{AuH}_2][\text{Cu}(\text{NH}_3)_2] \cdots [\text{Cu}(\text{NH}_3)_2][\text{AuH}_2]$ (**8**) (see Fig. 1). For model (8) we have included a tetramer having a cuprophilic Cu–Cu interaction. Such interaction has been described in previous theoretical work [5,23].

We first fully optimized the monomeric structures at the second-order Møller–Plesset perturbation theory (MP2) level. We used these geometries to study the metal–metal intermolecular interactions in the dimeric and tetrameric models (**1–8**) described above. The counterpoise correction for the basis-set superposition error (BSSE) was used for the calculated interaction energies.

The calculations were carried out using the Gaussian 03 program package [24]. For Au and Cu, the 19 and 10 valence-electron (VE) quasi-relativistic (QR) pseudo-potential (PP) of Andrae were employed, respectively [25]. The use of *f* orbitals is necessary when studying inter- and intramolecular interactions, as it has been previously shown for both atoms [5]. We employed two *f*-type polarization functions for a more accurate description of the interaction energy. The C, N and Cl atoms were treated through PPs, using double-zeta basis sets with the addition of one d-type polarization function [26]. For the H atom, a double-zeta basis plus one p-type polarization function was used [27].

We studied the intermolecular interactions by comparing the Au–Cu, Au–Au and Cu–Cu distances obtained at the HF and MP2

Table 2
Optimized Au–Cu distance, R_e , for the dimer and tetranuclear models at the MP2 and HF levels.

System	Method	R_e	$V(R_e)$	$\Delta E(\text{MP2-HF})^a$
$[\text{Au}(\text{C}_6\text{H}_5)_2] \cdots [\text{Cu}(\text{py})_2(\text{NCH})]$ (1)	MP2	259.1	–216.5	–32.0
	HF	271.6	–189.2	
$[\text{Au}(\text{C}_6\text{H}_5)_2] \cdots [\text{Cu}(\text{NCH})_2]$ (2)	MP2	272.2	–348.8	–31.2
	HF	311.5	–333.2	
$[\text{AuH}_2] \cdots [\text{Cu}(\text{NH}_3)_2]$ (3)	MP2	270.0	–392.4	–50.4
	HF	290.9	–347.3	
$[\text{AuCl}_2] \cdots [\text{Cu}(\text{NH}_3)_2]$ (4)	MP2	279.4	–344.9	–43.9
	HF	302.9	–305.7	
$[\text{Cu}(\text{NCH})_2][\text{Au}(\text{C}_6\text{H}_5)_2] \cdots [\text{Au}(\text{C}_6\text{H}_5)_2][\text{Cu}(\text{NCH})_2]$ (5)	MP2	274.0	–64.9	–33.4
	HF	^b		
$[\text{Cu}(\text{NH}_3)_2][\text{AuH}_2] \cdots [\text{AuH}_2][\text{Cu}(\text{NH}_3)_2]$ (6)	MP2	297.4	–2.6	–50.8
	HF	^b		
$[\text{Cu}(\text{NH}_3)_2][\text{AuH}_2] \cdots [\text{Cu}(\text{NH}_3)_2][\text{AuH}_2]$ (7)	MP2	296.6	–36.6	–24.7
	HF	370.3	–23.3	
$[\text{AuH}_2][\text{Cu}(\text{NH}_3)_2] \cdots [\text{Cu}(\text{NH}_3)_2][\text{AuH}_2]$ (8)	MP2	^b		
	HF	^b		

Equilibrium distance R_e in pm; interaction energy $V(R_e)$ in kJ/mol.

^a MP2 equilibrium distance.

^b No minimum.

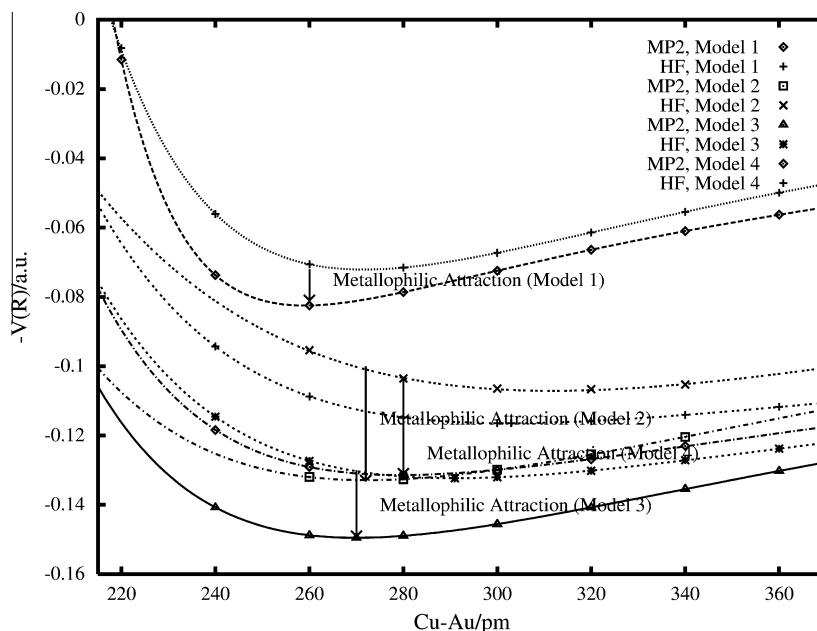


Fig. 2. HF and MP2 potential energy curves for $[\text{Au}(\text{C}_6\text{H}_5)_2] \cdots [\text{Cu}(\text{py})_2(\text{NCH})]$ (1), $[\text{Au}(\text{C}_6\text{H}_5)_2] \cdots [\text{Cu}(\text{NCH})_2]$ (2), $[\text{AuH}_2] \cdots [\text{Cu}(\text{NH}_3)_2]$ (3), and $[\text{AuCl}_2] \cdots [\text{Cu}(\text{NH}_3)_2]$ (4).

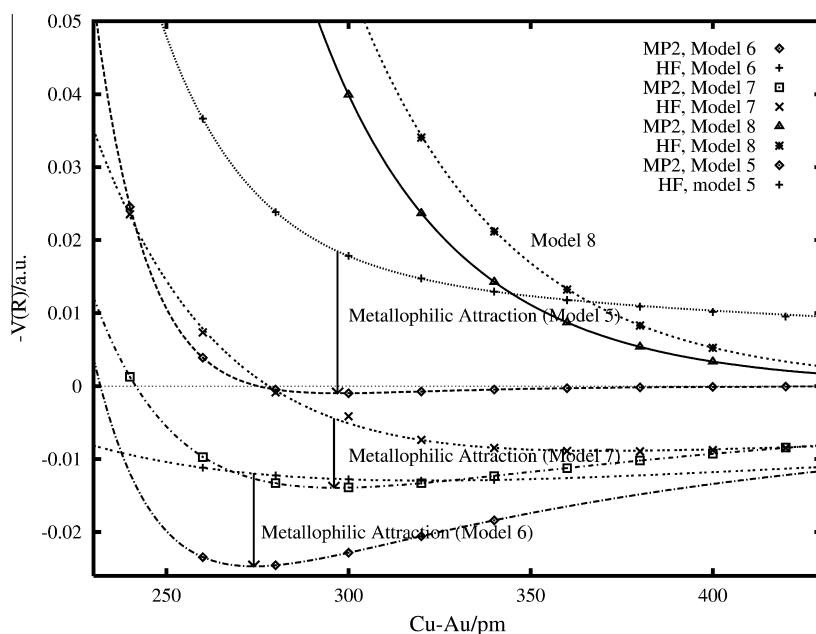


Fig. 3. HF and MP2 potential energy curves for $[\text{Cu}(\text{NCH})_2][\text{Au}(\text{C}_6\text{H}_5)_2] \cdots [\text{Au}(\text{C}_6\text{H}_5)_2][\text{Cu}(\text{NCH})_2]$ (5), $[\text{Cu}(\text{NH}_3)_2][\text{AuH}_2] \cdots [\text{AuH}_2][\text{Cu}(\text{NH}_3)_2]$ (6), $[\text{Cu}(\text{NH}_3)_2][\text{AuH}_2] \cdots [\text{Cu}(\text{NH}_3)_2][\text{AuH}_2]$ (7), and $[\text{AuH}_2][\text{Cu}(\text{NH}_3)_2] \cdots [\text{Cu}(\text{NH}_3)_2][\text{AuH}_2]$ (8).

levels. We have shown in several Au–Au, Au–Tl, Au–Ag and Au–Bi type systems that the nature of intra- and intermetallic interactions can be studied by comparison of HF and MP2 calculations [12–18]. Thus, if dispersion interactions are present in a system and electronic correlation effects are included, a shortening of the distance between the metal centers is observed when HF and MP2 calculations are compared. Although it is known that the MP2 approximation exaggerates the attractive interactions, this method gives a good indication of the existence of some type of interaction [28,29]. Of course, a more accurate method would be CCSD(T) (coupled cluster single, double and triple excitations) as was shown by Kaltsoyannis and Schwerdtfeger [30,31], but it is

very time consuming for the study of systems like the proposed models 1–8.

3. Results and discussion

We have used the experimental structures (see Table 1) through idealized dimeric and tetrameric models 1–8. In Table 2 we summarize the Au–Cu, Au–Au and Cu–Cu interaction energies ($V(R_e)$) and equilibrium distances (R_e). The calculated distances fall in the same range as the experimental ones. Using quasi-relativistic pseudo-potentials, the Au–Cu distance at the HF level is larger than

Table 3
NBO Charge on metal in the models at the MP2 level.

System	Metal ₁	Metal ₂	Metal ₃	Metal ₄
[Au(C ₆ H ₅) ₂] \cdots [Cu(py) ₂ (NCH)] (1)	+0.0876	+0.0038		
[Au(C ₆ H ₅) ₂] \cdots [Cu(NCH) ₂] (2)	+0.0096	+0.5449		
[AuH ₂] \cdots [Cu(NH ₃) ₂] (3)	-0.2399	+0.4751		
[AuCl ₂] \cdots [Cu(NH ₃) ₂] (4)	+0.1202	+0.5246		
[Cu(NCH) ₂][Au(C ₆ H ₅) ₂] \cdots [Au(C ₆ H ₅) ₂][Cu(NCH) ₂] (5)	+0.5464	-0.0553	-0.0553	+0.5464
[Cu(NH ₃) ₂][AuH ₂] \cdots [AuH ₂][Cu(NH ₃) ₂] (6)	+0.4635	-0.3236	-0.3236	+0.4635
[Cu(NH ₃) ₂][AuH ₂] \cdots [Cu(NH ₃) ₂][AuH ₂] (7)	+0.4782	-0.2337	+0.4969	-0.3532

Metal_{*n*} (*n* = 1–4) corresponds to the metal center in each model from left to right.

that obtained at the MP2 level, the latter being much closer to the experimental values for models **1–4**. Model **1** tends to shorten the Au–Cu distance due to the simplified nature of the model. The energy magnitudes at the HF and MP2 levels are in the electrostatic interaction range. Fig. 2 shows the potential energy curves for both models. This magnitude of energy is due to opposite charges of the gold and copper fragments. If we consider the intermolecular metal–metal interaction and compare each model at the HF and MP2 levels ($\Delta E(\text{MP2-HF})$), thus allowing the correlation effects on the metal–metal distances to be estimated, the energy differences are 32.0 and 31.2 kJ/mol for models **1** and **2**, respectively. This magnitude is within the range of the dispersion-type van der Waals interactions with charge transfer, similar to that found for the model [Ti(bipy)₂][Au(C₆H₅)₂] [17].

When we use simplified models such as **3–4**, this energy difference increases to 50.4 kJ/mol and 43.9 kJ/mol, respectively. However, the interactions found in models **1** and **2** are maintained qualitatively.

The MP2 calculation is able to reproduce the structural trends found in the experimental data. Thus, the interaction energy at MP2 level is composed by 87%, 95%, 89%, and 89% ionic interaction, and 13%, 5%, 11%, and 11% van der Waals interactions for models **1–4**, respectively. It is assumed that the ionic interaction is responsible for the attractive behavior obtained at the HF level. The additional stabilization obtained at the MP2 level is due to the introduction of dispersion-type correlation effects and charge transfer contributions. This situation differs to the in systems of the type Au–Ti, Au–Ag and Au–Bi as the ionic component is about 80%. The Au–Cu systems studied here are more ionic. We can conclude that dimeric models describe well the behavior observed for the Au–Cu attraction. Thus, it can be used to describe more complex systems like the tetranuclear ones.

We have built two groups of linear tetramer units. The first group is built through the interaction between two Au–Au dimers (models **5,6**). The second group is built through the interaction between Au–Cu and Cu–Cu fragments (**7,8**). Fig. 3 shows the potential curves at the HF and MP2 levels for these interactions. The results are summarized in Table 2. At the HF level there is no energy minimum in any of the models. This is because both fragments are neutrally charged.

Models **5** and **6** show a classic metallophilic interaction between the gold atoms. In models **1** and **2** the distances and interaction energies are found to be shorter and more stable than in systems **5** and **6**. These models represent the experimental complex [Au(C₆F₅)₂]₂[Cu(NCPh)₂]₂. Model **6** is more streamlined, with greater repulsion in the curve at the HF level. This is expressed with an energy difference of 50.8 kJ/mol between HF and MP2, while for model **5** it is 33.4 kJ/mol. The latter is very close to models **1** and **2**.

If we take into account the electronic correlation effects, the [+–+–] (**5,6**) system (33.4 and 50.8 kJ/mol) is found to be more stable, followed by [+–+–] (**7**) (24.7 kJ/mol), and finally [–++–] (**8**) (no minimum). For model (**8**), we were unable to obtain the cupro-

philicity as had been reported in other theoretical systems [23,33]. On the other hand, a similar result is observed experimentally for compound [Au(C₆F₅)₂]₂[Cu(NCPh)₂]₂ [14] with the sequence [+–+–] and an analogous result was found theoretically with models such as [Ti(bipy)₂]₂[Au(C₆F₅)₂]₂ and {[H₃P]₂Au}⁺[AuCl₂][–]]₂, succeeding in reproducing a [+–+–] experimental pattern [20,32].

If we take into account the electronic correlation effects into account, all the systems are stabilized by a similar amount of energy ($\Delta E(\text{MP2-HF})$). The ionic term is the one that displays the difference. The most stable situation is found for model (**5**) [+–+–] followed by model (**6**) and finally model (**7**) [+–+–].

If we focus on the natural bond orbital (NBO) [34] population of Au, Cu and the fragments, it is easier to understand the ionic effects on the different models (Table 3). The data for all the models show a reduction of the formal oxidation state for gold and copper. The smallest charge is found on gold in the calculated models, while a larger positive charge is concentrated on the copper centers. However, in all the models, we find the same magnitude of charge on the metallic atoms, which would give rise to a repulsive interaction. The total charge on the fragments is of opposite sign, thus allowing electrostatic interaction. Models (**1**) and (**5**) show the smallest repulsion among the neighboring metal centers. This effect is clearly due to the –C₆H₅ group in the gold fragment.

4. Conclusions

The present study provides further information about the nature of the interactions in the Au–Cu in dimer and tetranuclear models. We found that the interactions are due mainly to an ionic effect, enhanced by an electronic correlation term. Both effects are important when we consider the training of the polymer from smaller units. The most stable energy is found for the [+–+–] pattern, analogous to the experimental arrangement.

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