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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.

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 $[AuR_2]^-$ ($R = -C_6F_5$, $-C_6F_3Cl_2$ and $-C_6Cl_5$) to react with Lewis acid metal salts, what allows us to isolate complexes bearing unsupported Au(I)···M interactions (M = 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 $[AuR_2]^-$ ($R = C_6F_5$ or C_6Cl_5) (Lewis bases), provides an additional electrostatic attraction [20]. We have succeeded in synthesizing Au–Tl complexes by reacting a $[AuR_2]^-$ 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 $[Tl(bipy)_2][Au(C_6F_5)_2]$ [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 wihich 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 $[Au(C_6F_5)][Cu(NCCH_3)$-μ_2-$C_4H_4N_2)]_n$, $[Au(C_6F_5)_2][Cu(NCCH_3)_2]$, $[Au(C_6F_5)_2][Cu(NCCHCHPh)_2]$ and $[Au(C_6F_5)_2]_2[Cu(NCPh)_2]_2$ [14,15]. These complexes show

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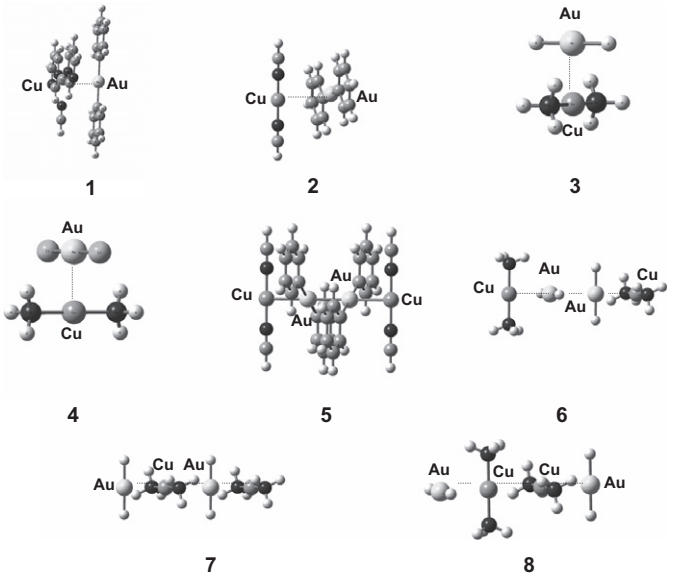

Fig. 1. Theoretical model systems.

unsupported Au(I)···Cu(I) metallophilic interactions and interesting photophysical properties. The solid state crystal structure of the complex $[Au(C_6F_5)_2]_2[Cu(NCPh)_2]_2$ 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 $[Tl(bipy)_2][Au(C_6F_5)_2]$ 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 $[Au(C_6F_5)][Cu(NCCH_3)(\mu_2\text{-}C_4H_4N_2)]_n$, $[Au(C_6F_5)_2][Cu(NCCH_3)_2]$, $[Au(C_6F_5)_2][Cu(NCCHCHPh)_2]$ and $[Au(C_6F_5)_2]_2[Cu(NCPh)_2]_2$ [14,15] were used to build theoretical models, which are depicted in Fig. 1. The original F–, $-NCCH_3$, –NCPh and μ_2-$C_4H_4N_2$ ligands were replaced by H–, Cl–, –NCH and C_5H_5N–. 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: $[Au(C_6H_5)_2]\cdots[Cu(py)_2(NCH)]$ **(1)**, $[Au(C_6H_5)_2]\cdots[Cu(NCH)_2]$ **(2)**; $[AuX_2][Cu(NH_3)_2]$ **(3,4)** X = H,Cl; $[Cu(NCH)_2][Au(C_6H_5)_2]\cdots[Cu(NCH)_2][Au(C_6H_5)_2]$ **(5)**; $[Cu(NH_3)_2][AuH_2]\cdots[AuH_2][Cu(NH_3)_2]$ **(6)**; $[Cu(NH_3)_2][AuH_2]\cdots[Cu(NH_3)_2][AuH_2]$ **(7)** and $[AuH_2][Cu(NH_3)_2]\cdots[Cu(NH_3)_2][AuH_2]$ **(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 1
Experimental values for the metallophilic attraction from crystal-structures.

System	Au–Cu/pm	Au–Au/pm
$[Au(C_6F_5)_2][Cu(NCCH_3)_2]$ [14]	293.4	
$[Au(C_6F_5)_2][Cu(CNPh)_2]$ [14]	267.3	
$[Au(C_6F_5)_2]_2[Cu(NCCH=CHPh)_2]_2$ [14]	261.6	300.1
	260.9	
$[Au(C_6F_5)][Cu(NCCH_3)(\mu_2\text{-}C_4H_4N_2)]_n$ [15]	282.2	

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

System	Method	R_e	$V(R_e)$	ΔE(**MP2-HF**)[a]
$[Au(C_6H_5)_2]\cdots[Cu(py)_2(NCH)]$ **(1)**	MP2	259.1	−216.5	−32.0
	HF	271.6	−189.2	
$[Au(C_6H_5)_2]\cdots[Cu(NCH)_2]$ **(2)**	MP2	272.2	−348.8	−31.2
	HF	311.5	−333.2	
$[AuH_2]\cdots[Cu(NH_3)_2]$ **(3)**	MP2	270.0	−392.4	−50.4
	HF	290.9	−347.3	
$[AuCl_2]\cdots[Cu(NH_3)_2]$ **(4)**	MP2	279.4	−344.9	−43.9
	HF	302.9	−305.7	
$[Cu(NCH)_2][Au(C_6H_5)_2]\cdots[Au(C_6H_5)_2][Cu(NCH)_2]$ **(5)**	MP2	274.0	−64.9	−33.4
	HF	[b]		
$[Cu(NH_3)_2][AuH_2]\cdots[AuH_2][Cu(NH_3)_2]$ **(6)**	MP2	297.4	−2.6	−50.8
	HF	[b]		
$[Cu(NH_3)_2][AuH_2]\cdots[Cu(NH_3)_2][AuH_2]$ **(7)**	MP2	296.6	−36.6	−24.7
	HF	370.3	−23.3	
$[AuH_2][Cu(NH_3)_2]\cdots[Cu(NH_3)_2][AuH_2]$ **(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.