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Theoretical study of the aggregation of d^{10}–s^2 Au(I)–Tl(I) complexes in extended unsupported chains

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Abstract

Model compounds are used to study the metallophilic attraction between gold and thallium atoms. Ab initio calculations on dimers and tetramers in different distributions of the minimal units are analyzed. An attraction is found for all models and there is a reasonable agreement between the experimental and theoretical geometries at the HF and MP2 levels.
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1. Introduction

In the last years the bonding interaction between closed-shell metal atoms have been widely studied from theoretical and experimental points of view [1,2]. Among the heavy metal atoms are the gold–gold interactions (aurophilicity) the ones which have received most attention. Also, in the last times it can be found in the literature gold(I)-containing heterometallic systems in which short closed-shell metal–metal interactions are present (metallophilicity) [3–6]. Thus, for example, Au^I–Pd^{II} (d^{10}–d^8) [7], Au^I–Ag^I (d^{10}–d^{10}) [8], Au^I–Cu^I (d^{10}–d^{10}) [8] and Au^I–Tl^I (d^{10}–s^2) [9–11] interactions have been theoretically described using correlated methods and it has been shown that the metallophilic interactions arise from dispersion-type correlation effects (van der Waals) and charge transfer contributions [11].

The formation of Au–M interactions based on acid–base reactions like, for instance, Tl^+ or Ag^+ Lewis acids precursors with $[AuR_2]^-$ ($R = C_6F_5$ or C_6Cl_5) Lewis bases, provides an additional electrostatic attraction [12]. On the other hand, some of these Au^I–metal complexes have been revealed as a new class of photoluminescent materials in which the emission of radiation results mainly from the interactions between the different metal centres [13].

We have succeeded in the synthesis of Au–Tl complexes through the use of $[AuR_2]^-$ Lewis base precursors against Tl^+ salts acting as Lewis acids [9–11]. Thus, we have reported the synthesis and luminescent behaviour of the first unsupported gold–thallium chain [Tl(OP-Ph$_3$)$_2$][Au(C$_6$F$_5$)$_2$] [11] and new two- and three-dimensional arrays of the type [Tl(4,4'-bipy)$_n$][AuR$_2$] ($R = C_6F_5$ and C_6Cl_5; 4,4'-bipy = 4,4'-bipyridine) [12], in which the change of the perhalophenyl ligands gives rise to different structural arrangements. From a theoretical point of view, the metallophilicity between gold(I) and thallium(I) centres in these compounds gives an average metal–metal

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separation of 300 pm and the interaction energy is estimated at about 276 kJ/mol, of which 80% are of an ionic origin [11].

When examining the details of the supramolecular chemistry of the [Tl(bipy)$_2$][Au(C$_6$F$_5$)$_2$]$_2$ [12] in the solid state, the complex consists of a planar polymer arrangement formed by a Tl–Au–Au–Tl metal disposition following the pattern [+−−+] for the fragment charges. This situation is at variance with the simple rules of Coulomb forces. While under certain experimental conditions, it is possible to obtain the common pattern [−+−+] and [−++−] [21].

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}–s^2 Au^I···Tl^I interaction for di- and tetra-nuclear species. This permitted us to understand the forces that operate in the building up of the supramolecular arrangements in the solid state.

2. Models and computational details

The Gaussian 03 package [14] was used. The following basis sets and pseudopotentials (PP) were used: the 19-valence electron (VE) and 3-VR quasi-relativistic (QR) pseudopotential (PP) were employed for gold and thallium, respectively [15,16]. We have employed two *f*-type polarization functions for Au and Tl centres. The *f* orbitals are necessary for the weak intermolecular interactions, as was demonstrated previously for various metals [8,11]. Carbon and nitrogen atoms were also treated by Stuttgart pseudopotentials [17], including only the valence electrons for each atom. For carbon and nitrogen atoms, double-zeta basis sets were used, augmented by *d*-type polarization functions; for the H atom, a double-zeta plus one *p*-type polarization function was used [18].

First, we studied the experimental compounds through the model [Tl(bipy)$_2$][Au(C$_6$H$_5$)$_2$]. We replaced the groups –C$_6$F$_5$ by –C$_6$H$_5$. We optimized the structures [Tl(bipy)$_2$]$^+$
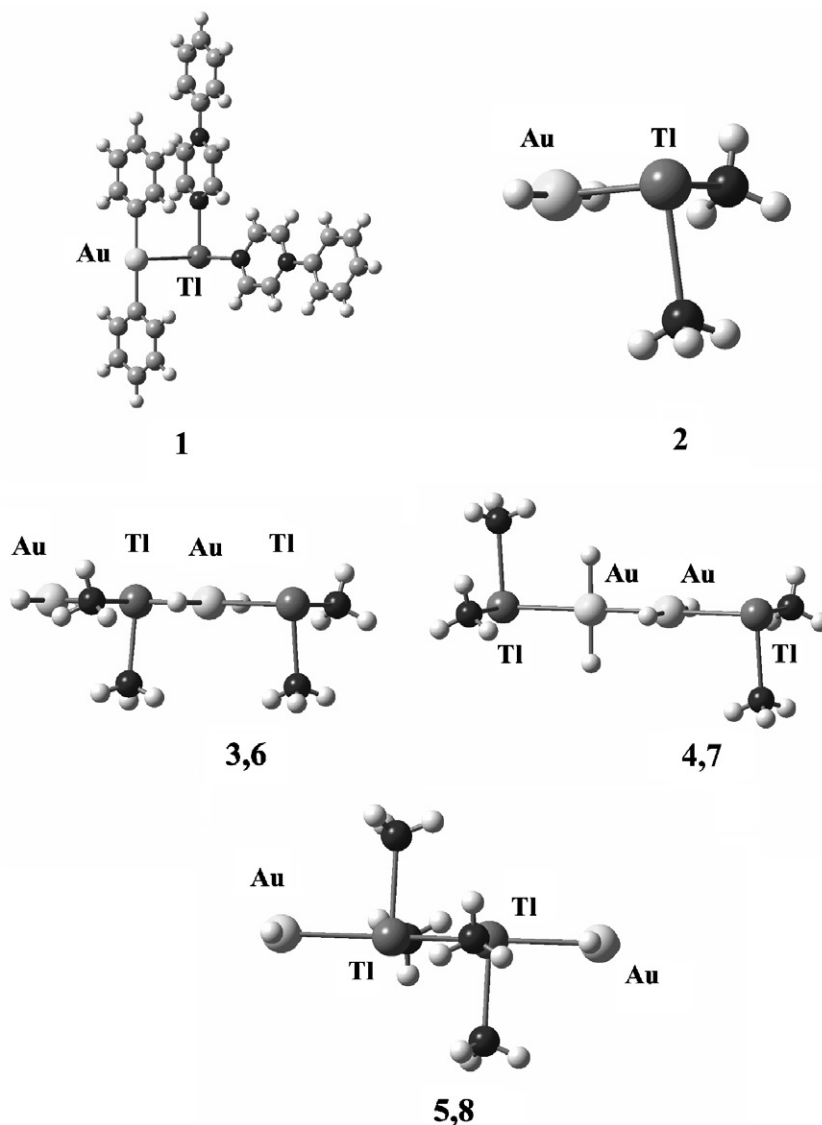
Fig. 1. Theoretical model systems.