

# Ab initio study of the structure and stability of $M_nTl_n$ ( $M = Cu, Ag, Au; n = 1, 2$ ) clusters

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## Abstract

The small coinage-metal thallium compounds  $MTl$  and  $M_2Tl_2$  ( $M = Cu, Ag,$  and  $Au$ ) are studied at HF, MP2 theoretical level with relativistic pseudopotentials. It is found that the butterfly structure with  $C_{2v} (^1A_1)$  symmetry for  $M_2Tl_2$  ( $M = Cu, Ag,$  and  $Au$ ) is more stable than planar structures and the  $Au_2Tl_2$  is the most stable cluster. The atomization energies and the HOMO–LUMO gap are evaluated, which indicates that doping clusters  $M_2Tl_2$  are more stable than the pure clusters  $M_4$ . The electron correlation effects on geometrical structures are investigated which compact and stabilize the present species. Theoretical results of the structure and the bond lengths for  $Au_2Tl_2$  are in good agreement with experimental results available.

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**Keywords:** Coinage-metal thallium compounds; MP2 theoretical level; Atomization energies; Electron correlation effects

## 1. Introduction

Bimetallic clusters have attracted the attention of chemists and physicists over the last two decades [1–3]. They found that when doping pure metals or metal surfaces with metallic heteroatoms, the new system often exhibits more favorable properties for applications than the non-doped pure metals. Over the past two decades a few studies, both theoretical and experimental, of coinage metal clusters doping the group III element have been reported. For example, Miroslav et al. [4] studied the binding of aluminum to coinage metals at CCST(T) theoretical level and it indicated that the electron correlation and relativistic effects play an important role. Rajendra et al. [5] obtained the candidate structures for the ground-state geometry of  $Al_2M$  and  $Al_3M$  ( $M = Cu, Ag,$  and  $Au$ ) clusters within the spin-polarized density-functional theory with a three-parameter hybrid function to describe the exchange-correlation effects and found that the atomization energies are

substantially larger for the coinage metal atom to pure Al clusters. Experimentally, in 1992 Yamada et al. [6] produced metal alloy clusters including  $Cu_nAl_m$ ,  $Cu_nIn_m$ ,  $Ag_nAl_m$  and  $Ag_nIn_m$  by a gas aggregation source and investigated by time-of-flight mass spectrometry following ionization with a KrF excimer laser. In 1999 Heinebrodt et al. [7] studied the bonding character of  $Au_nX_m$  ( $X = Al, In$ ) clusters using time-of-flight mass spectrometry. The mass spectra of gold–aluminum clusters exhibit electronic shell effects for arbitrary composition. W. Bouwen and co-workers [8] reported the stability effects of  $Au_nX_m^+$  ( $X = Cu, Al, Y,$  and  $In$ ) clusters. In 2001 and 2003 M. Kumar [9,10] studied formation of aqueous  $Tl/Ag$  and  $Tl/Cu$  bimetallic clusters by gamma and electron irradiation. In the most recent paper [11], the new tetranuclear complexes  $[Au_2Tl_2(C_6Cl_5)_4] \cdot L$  ( $L = PhMeC=O,$   $acacH$ ) or  $[Au_2Tl_2(C_6Cl_5)_4(bipy)] \cdot (acacH)$  have been prepared by treatment of the polymeric species  $[AuTl(C_6Cl_5)_2]_n$  with ketones or with acetylacetone and 4,4'-bipyridine. Their crystal structures determined by X-ray diffraction methods present a central  $Au_2Tl_2$  core formed via one  $Tl-Tl$  and four  $Au-Tl$  unsupported interactions resulting in a loosely

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bound butterfly cluster. To our knowledge, no theoretical works for the  $M_2Tl_2$  ( $X = Cu, Ag, \text{ and } Au$ ) clusters have been found.

In present study, we have systematically investigated the tetraatomic species  $M_2Tl_2$  ( $M = Cu, Ag, \text{ and } Au$ ) to shed light on the geometrical structures, stabilities using quantum-mechanical calculations with the substitution of two  $M$  atoms by two  $Tl$  atoms in the  $M_4$  cluster. Atomization energies, the HOMO energy, LUMO energy and HOMO–LUMO gap have been evaluated. The calculated structures are compared with the experimental structures available.

## 2. Methods

The coinage-metal atoms  $M$  ( $M = Cu, Ag, \text{ and } Au$ ) were treated with 19-valence electron (EV) relativistic PPs with corresponding basis sets (8s7p6d)/[6s5p3d] given by Dolg et al. [12] and Andrae et al. [13]. For the coinage-metal atoms, Pyykkö et al. [14] pointed out that the diffuse  $f$  function is required for describing covalent bond. Therefore, the  $f$ -type diffuse functions, which  $\alpha_f = 0.20$  for  $Au$ ,  $\alpha_f = 0.22$  for  $Ag$  and  $\alpha_f = 0.24$  for  $Cu$ , were added to yield an overall basis set of (8s7p6d1f)/[6s5p3d1f], respectively. The LANL2DZ basis set was used to describe the  $Tl$  atom.

The geometries of present systems were calculated at MP2 theoretical level. In order to examine the suitability of the MP2 method and the PPs for the present species, the bond lengths, vibrational frequencies and dissociation energies of diatomic molecules  $M_2$  ( $M = Cu, Ag, \text{ and } Au$ ) calculated at HF, MP $n$  ( $n = 2–4$ ), CCSD and CCSD (T) levels are compared with experimental data [15–18] in Table 1. The post-HF methods were used to describe the electron correlations effects. It can be seen from Table 1 that our calculated MP2 and CCSD (T) geometry ( $r$ ), vibrational frequency ( $\nu$ ), and dissociation energy ( $D_e$ ) values are in good agreement with the known experimental data. The MP2 geometries and dissociation energies are even more accurate than CCSD (T) values, while vibrational frequencies are only slightly larger. The calculated results for  $Tl_2$  are also reported in Table 1. The paper [19] in which the dissociation curves were computed for the ground states of  $Tl_2$  from relativistic effective potential calculations indicated that  $Tl_2$  is only weakly bound which is in good agreement with the calculated dissociation energy ( $D_e$ ) value 0.8197 eV at MP2 level in this paper. The comparison indicates that the MP2 method is sufficiently accurate, and essentially can reflect the electron correlations effects within the theoretical levels of performing calculations with above the methods. Therefore, for  $M_2Tl_2$  ( $M = Cu, Ag, \text{ and } Au$ ) clusters were investigated at MP2 theoretical level because of limitations in our computer resource. Furthermore, our previous studies [20–23] proved that the present PPs and corresponding basis set is sufficiently accurate to investigate  $Cu, Ag, \text{ and } Au$  containing clusters.

Table 1  
Optimized geometries  $r$  (Å), vibrational frequencies  $\nu$  ( $cm^{-1}$ ), HOMO–LUMO gap  $E_{gap}$ (eV) and dissociation energies  $D_e$  (eV) for  $M_2$  ( $M = Cu, Ag, \text{ and } Au$ ) and  $Tl_2$  molecules

Species	Methods	$r$	$\nu$	$E_{gap}$	$D_e$
$Cu_2$	HF	2.374	203.7	6.5852	0.5479
	MP2	2.211	293.5	6.8015	2.0050
	MP3	2.268	250.1	6.7261	1.6257
	MP4	2.188	322.1	6.8306	2.0232
	CCSD	2.239	270.7	6.7656	1.8872
	CCSD (T)	2.230	276.7	6.7765	2.0569
	Exp. <sup>a</sup>	2.197			2.010
$Ag_2$	HF	2.708	149.3	6.1280	0.4212
	MP2	2.565	198.5	6.3106	1.7374
	MP3	2.595	187.4	6.2728	1.5966
	MP4	2.567	198.9	6.3095	1.6729
	CCSD	2.590	188.3	6.2800	1.6294
	CCSD (T)	2.585	189.7	6.2858	1.7429
	Exp.	2.530 <sup>b</sup>	192.0 <sup>b</sup>		1.66 <sup>c</sup>
$Au_2$	HF	2.624	154.0	7.2733	0.7114
	MP2	2.537	186.4	7.4630	2.3056
	MP3	2.567	175.8	7.3971	2.0156
	MP4	2.543	183.9	7.3971	2.1110
	CCSD	2.561	177.5	7.4110	2.1060
	CCSD (T)	2.560	177.5	7.4129	2.2287
	Exp. <sup>d</sup>	2.472			2.29
$Tl_2$	HF	3.176	81.7	4.6134	0.5469
	MP2	3.127	85.0	4.6428	0.8197
	MP3	3.159	80.8	4.6232	0.8044
	MP4	3.166	79.2	4.6189	0.8054
	CCSD	3.172	78.4	4.6153	0.8040
	CCSD (T)	3.177	77.0	4.6123	0.8368

<sup>a</sup> Ref. [15].

<sup>b</sup> Ref. [16].

<sup>c</sup> Ref. [17].

<sup>d</sup> Ref. [18].

The calculations were performed with the Gaussian 98 W program package [24].

## 3. Results and discussion

### 3.1. Geometry and stability

#### 3.1.1. $MTl$ ( $M = Cu, Ag, \text{ and } Au$ ) series

The calculated total energy, bond lengths, vibrational frequency, the HOMO–LUMO gap, and dissociation energy of  $MTl$  calculated at various theoretical levels (HF, MP $n$  ( $n = 2–4$ ), CCSD, CCSD (T)) are shown in Table 2. To our knowledge, for these series no experimental or previous theoretical data exist to compare our values. Table 2 shows that the bond lengths, vibrational frequencies and dissociation energies of  $MTl$  calculated at MP2 level are almost identical with that calculated at CCSD (T) level. The calculations indicate that the  $^1\Sigma^+$  state is the ground state. It can be seen from Tables 1 and 2 that the bond length, vibrational frequency, and the HOMO–LUMO gap of the  $MTl$  ( $M = Cu, Ag, \text{ and } Au$ ) dimer have an intermediate value with respect to those of  $M_2$  and  $Tl_2$

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