Nano-jewellery: C_5Au_{12}—a gold-plated diamond at molecular level

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A mixed carbon-metal cluster is designed by combining the tetrahedral C_5 radical (with a central atom—the skeleton of the C_5H_{12} molecule) and the spherical Au_{12} layer (the external atomic shell of the Au_{13} cluster). The C_5Au_{12} cluster and its negative and positive ionic derivatives, $C_5Au_{12}^{\pm}$, are investigated *ab initio* (DFT) in terms of optimized structures and relative energies of a few spin-states, for the icosahedral-like and octahedral-like isomers. The cluster is predicted to be generally more stable in its octahedral shape (similar to C_5H_{12}) which prevails for the negative ion and may compete with the icosahedral shape for the neutral system and positive ion. Adiabatic ionization energies (AIE) and electron affinities (AEA) of C_5Au_{12}, vertical electron-detachment (VDE) energies of $C_5Au_{12}^-$, and vertical ionization and electron-attachment energies (VIE, VEA) of C_5Au_{12} are calculated as well, and compared with those for the corresponding isomers of the Au_{13} cluster. The AIE and VIE values are found to be close for the two systems, while the AEA and VDE values are significantly reduced for the radical-based species. A simple fragment-based model is proposed for the decomposition of the total interaction into carbon–gold and gold–gold components.

1 Introduction

Gold clusters are of interest from both fundamental and practical viewpoints. Fundamentally, they are species intermediate in size between separate atoms and bulk metal and thus potentially have different properties. Practically, they serve, in particular, as catalytic agents for chemical reactions (*e.g.* reduction of air pollution)[1] and as nano-sized electrodes interfacing molecules in nano-electronic devices.[2] Among other clusters, a stable isomer of Au_{13} has been predicted[3,4] (from calculations without geometry constraints) to follow the optimal close-packing of hard spheres and to have an icosahedral structure (Fig. 1a). Consistent with this, the larger, Au_{20} cluster has been found[5] to have a regular tetrahedral structure (incorporating icosahedral Au_{13}) which reproduces that of the macroscopic crystal fragment. Other isomers of Au_{13}, comparatively or even more stable, include, in particular, cuboctahedral (hereafter called octahedral) shown in Fig. 1b and asymmetric (amorphous) clusters.[3,4]

Doping of metal clusters with different atoms can modify the clusters' structural, chemical (catalytic), and other characteristics, and may lead to new species with unique properties of interest. Ideally, this would eventually allow the design of clusters with predetermined parameters. Recent studies[6,7] have addressed doping of Au_{12} with a different metal atom, such as W and Mo. The structure of such a system exhibits a non-Au (W, Mo) atomic core M in the twelve-atom icosahedral gold shell. Octahedral isomers have been found for MAu_{12} as well, with higher energies relative to the icosahedral ones.

The purpose of this paper is to investigate a gold cluster with another, non-metal core in a similar Au_{12} shell. The tetrahedral C_5 radical with a central atom (Fig. 2a) has been chosen as a molecular dopand due to its four peripheral C atoms with twelve (three per atom) valence electrons available to form bonds with twelve (monovalent) Au atoms of the gold shell, with a potential for generating a closed-shell electronic structure. Furthermore, both icosahedral and octahedral shells are formed by four equilateral triangular groups of atoms in a tetrahedral arrangement around the shell centre, thus matching the symmetry of the C_5 core when it is placed in the centre. Since tetrahedral C_5 is a structural unit of the diamond crystal lattice, the resulting C_5Au_{12} cluster can be viewed, at molecular level, as a gold-plated diamond. Earlier work has addressed smaller ionic clusters including CAu_n^{m+} (n = 4–6), at a Hartree–Fock level.[8]

2 Computational tools and methods

All calculations have been carried out using the NWChem package[9] and all pictures produced with the Molekel molecular graphics package.[10] Density functional theory has been employed, in accord with earlier work[6,7] on metal-doped MAu_{12}, with the B3LYP hybrid functional, the 6-31G* basis set for the C atom and the LanL2DZ effective core potential (ECP) with corresponding basis set for the Au atoms. A few

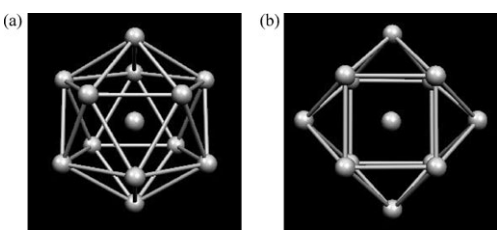

Fig. 1 (a) Icosahedral and (b) octahedral isomers of the Au_{13} cluster.

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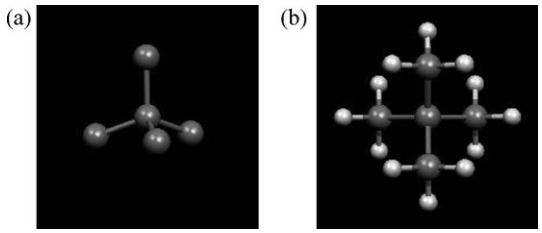

Fig. 2 (a) C_5 skeleton; (b) C_5H_{12} (tetramethylmethane) molecule.

calculations have been done with a larger, Stuttgart group's RSC basis set (with ECP) as well.

The lowest energy states of neutral and ionic species have been geometry-optimized for a few spin multiplicities. An all-atom optimization has been performed for every case, in the C_1 symmetry group, thus avoiding additional geometry constraints which might otherwise lead to false stable geometries. Vibrational frequencies have been evaluated to verify the optimized structures to correspond to energy minima. These structures may represent local energy minima as the explored configurational space has been limited. Its expansion is the subject of future work.

Test calculations for the ground state Au_2 ($X\ ^1\sum_g^+$) dimer have resulted in the dissociation energy $D_e = 1.87$ eV at the equilibrium distance $R_e = 2.57$ Å, to be compared with the experimental values 2.31 eV and 2.47 Å, respectively. As a further comparison, spin-unrestricted UMP2 calculations with the same basis set yield 1.82 eV and 2.60 Å, thus predicting a slightly lower binding relative to DFT. The corresponding results for the ground state AuC ($X\ ^2\Pi$) molecule are $D_e = 1.97$ eV and $R_e = 1.88$ Å at the DFT, and 1.92 eV and 1.83 Å at the MP2 levels, respectively, showing a close match as well.

The "parent" icosahedral Au_{13} cluster has been optimized in its sextet ($S = 5/2$) spin state, as lower-spin states have not preserved the desired geometry. The resulting Au_{12} shell has then been employed in further calculations.

The C_5 radical represents the carbon skeleton of the tetramethylmethane (or dimethylpropane) molecule C_5H_{12} shown in Fig. 2b, with its C atoms sp^3-hybridized (approximately for the peripheral C atoms) and twelve H atoms terminating twelve bonds of four peripheral carbons. This molecule has been optimized in its ground state and the C_5 skeleton then used in constructing the C_5Au_{12} species.

3 Results and discussion

3.1 Neutral cluster

3.1.1 C_5Au_{12}. Two main structure types have been employed for the starting geometries of C_5Au_{12}: the shell-based one, with C_5 placed and appropriately oriented inside the Au_{12} shell, and the core-based type, with twelve Au atoms put on extensions of the C–H bonds in C_5H_{12}. The second type exhibits an octahedral-like geometry and thus correlates to the other, octahedral isomer of the Au_{13} cluster.

Considering, in first instance, C_5Au_{12} as a gold-based analogue of closed-shell C_5H_{12}, singlet states have been optimized first, for both the icosahedral- and octahedral-like

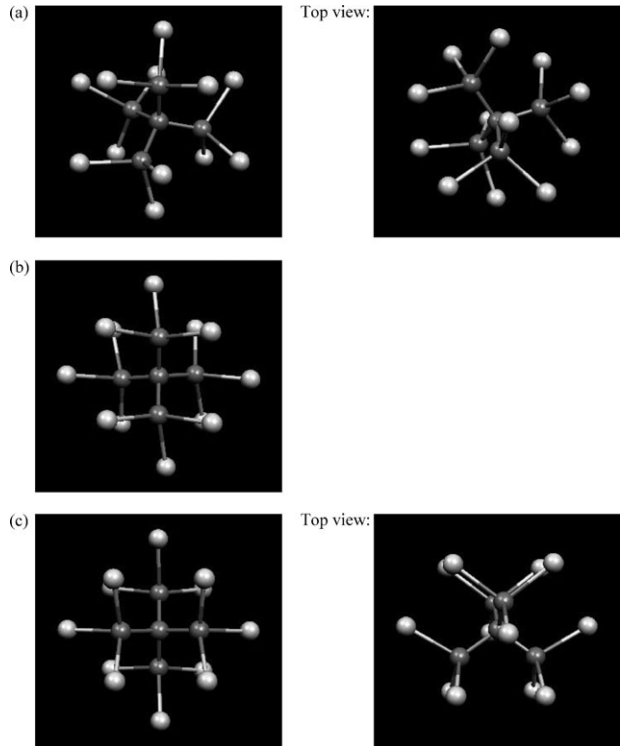

Fig. 3 Optimized geometries of C_5Au_{12}: (a) I_h-shaped isomer (singlet), front and top views; (b) O_h-shaped isomer (singlet); (c) O_h-shaped isomer (triplet), front and top views.

(hereafter I_h and O_h) isomers, with final structures shown in Fig. 3a and b. These structures are found to (approximately) keep their icosahedrally and octahedrally shaped gold shells, and their energies are only marginally different, the I_h isomer being $\sim$0.01 eV more stable. In both cases, each peripheral C atom of the C_5 core appears to be bonded to the nearest three Au atoms, and the (approximate) sp^3-hybridization of the C atoms is preserved.

The relative energies and equilibrium geometry parameters of both isomers are collected in Table 1, including the results for different spin states. For the I_h isomer, all central–peripheral C–C distances are 1.60 Å and all C–Au distances are 2.06 Å. The Au–Au distances are nearly equal (3.23 Å) for the three atoms bonded to one carbon, but are generally longer and vary within 10% ($\approx$ 3.2–3.5 Å) between nearest atoms bonded to different carbons, making the I_h structure an imperfect icosahedron. The calculated vibrational frequencies range from 24–854 cm^{-1} and are all real, indicating a local energy minimum. The zero-point vibrational energy is predicted to be 0.73 eV.

For the O_h isomer, the C–C and C–Au distances are the same (within 0.01 Å) and longer (within 0.05 Å), respectively, compared to the I_h isomer. However, opposite to the I_h case, the Au–Au distances in the same-carbon bonded gold triplets are different by about 10% (with values grouping near $\sim$3.1 and $\sim$3.4 Å), and are shorter and more even ($\sim$2.9–3.0 Å) between neighbouring gold atoms bonded to different carbons. The O_h structure is thus imperfect as well, being skewed towards a lower symmetry case (Fig. 3b). It exhibits a wider interval of Au–Au distances compared to the I_h structure.

Table 1 Calculated relative energies (in eV) and equilibrium distances (in Å) of C_5Au_{12} and $C_5Au_{12}^{\pm}$. Additional relative values for ions are italicized (with new zeros shown). The distances are given with variations (for different atom pairs): 3.23–4 is 3.23–3.24

	I_h	O_h
C_5Au_{12}		
$S = 0$	$E = 0$ $R_{C-C} = 1.600$ $R_{C-Au} = 2.065/3.104–8^b$ $R_{Au-Au} = 3.23–4^a/3.19, 3.50$	$E = +0.014$ $R_{C-C} = 1.59–60$ $R_{C-Au} = 2.06–11/3.08–14^b$ $R_{Au-Au} = 3.07–10, 3.36–40^a/2.88–98$
$S = 1$	$(\rightarrow)^c$	$E = +0.072$ $R_{C-C} = 1.59–63$ $R_{C-Au} = 2.07–8$ $R_{Au-Au} = 3.22–7^a/2.96–3.06$
$S = 1$		$E = -0.059$ $R_{C-C} = 1.58–61$ $R_{C-Au} = 2.07–09$ $R_{Au-Au} = 3.19, 3.28–33^a/2.89–96$
$S = 2$	$(\rightarrow)$	$E = +0.625$ $R_{C-C} = 1.57–60$ $R_{C-Au} = 2.08–13$ $R_{Au-Au} = 3.25–37^a/2.83–4, 2.94–5$
$C_5Au_{12}^-$		
$S = 1/2$	$(\rightarrow)$	$E = -2.839$ (= −AEA) *0* $R_{C-C} = 1.647, 1.605$ $R_{C-Au} = 2.08–9/3.09–18^b$ $R_{Au-Au} = 3.26–3.32^a/2.90–9$
$S = 3/2$	$(\rightarrow)$	*E = +0.609* $R_{C-C} = 1.59–60$ $R_{C-Au} = 2.07–15$ $R_{Au-Au} = 3.14–36^a/2.85–97$
$S = 5/2$		*E = +1.197*
$C_5Au_{12}^+$		
$S = 1/2$	$E = +5.964$ (= AIE) *0* $R_{C-C} = 1.58–61$ $R_{C-Au} = 2.05–7/3.05–14^b$ $R_{Au-Au} = 3.20\text{-}4^a/3.05–20$	*E = +0.083* $R_{C-C} = 1.580$ $R_{C-Au} = 2.083–5/3.094–6^b$ $R_{Au-Au} = 3.28–9^a/2.89–91$
$S = 3/2$	$(\rightarrow)$	$E = +5.962$ *−0.002* $R_{C-C} = 1.580$ $R_{C-Au} = 2.084–5$ $R_{Au-Au} = 3.283–5^a/2.899–902$
$S = 5/2$		*E = +0.791* $R_{C-C} = 1.56–8$ $R_{C-Au} = 2.07–12$ $R_{Au-Au} = 3.20–32^a/2.87–3.02$

[a] Distances between the gold atoms bonded to the same C atom (in the CAu_3 groups). [b] Distances between the Au atoms and the central C atom. [c] Arrow for an I_h isomer indicates that it transforms into the O_h isomer upon optimization.

The approximate charge distribution from the Mulliken populations exhibits alternating positive and negative layers, similar for both isomers: $+0.27 \pm 0.05$ *e* on the central and -0.45 ± 0.01 *e* on the terminal carbons, followed by $+0.13 \pm 0.01$ *e* on the gold atoms. The central atom is 0.1 *e* more positive for the O_h isomer. The C_5 core is thus negatively charged, which is different from Au_{13} (as well as WAu_{12}[11]) with its positively charged central atom and negatively charged surface atoms.

The corresponding triplet states are shifted in energy from the singlets slightly and almost equally (by ~0.07 eV) but in opposite directions (up for the I_h and down for the O_h isomer), and therefore show a more pronounced energy difference (≈ 0.13 eV), with the O_h isomer being more stable and thus representing the ground state. In fact, the original I_h isomer acquires a distorted octahedral shape (resembling that in Fig. 3b), thus transforming into another, higher energy triplet O_h-like isomer. For the O_h-originated (and shape-preserved) lower energy triplet state, the C–C and C–Au distances are 1.60 ± 0.01 and 2.08 ± 0.01 Å, respectively. The Au–Au distances are ~3.2 –3.3 Å within the CAu_3 groups, *i.e.* more even than for the (O_h-shaped) singlet state, and ~2.9–3.0 Å between the gold-neighbours from different groups (*i.e.* similar to singlet). The overall structure is more symmetric (Fig. 3c) compared to the singlet state. The Mulliken populations for the (ground state) triplet O_h isomer are essentially identical to that for the singlet case.

Upon optimization of the quintet states, both isomers converge to the same O_h-shaped structure about 0.6 eV higher in energy relative to the singlet state. The C–C, C–Au, and Au–Au distances are similar to those for the triplet state (Table 1). The overall trend with increasing the spin multiplicity is, however, the reduction of the variation interval of the Au–Au distances within the CAu_3 group—from ~0.3 to ~0.1 Å.

The lowest energy state is thus predicted to be singlet for the I_h isomer but triplet for the O_h isomer, the latter being more stable by ~0.06 eV only. Hence, C_5Au_{12} behaves differently from the C_5H_{12} counterpart in the sense of a more pronounced interaction between the Au atoms leading to the non-singlet ground state. The carbon core does, however, impose the overall geometry (according to the C–H bond orientations in the C_5H_{12} analogue), making the O_h isomer more stable, unlike the I_h isomer for MAu_{12}.

In order to detail the structural effect of replacing the central Au atom in Au_{13} by the C_5 core to form C_5Au_{12}, both corresponding isomers, I_h and O_h, of Au_{13} have also been calculated using the same level of theory (DFT method and Au basis set). For consistency, the sextet ($S = 5/2$) states have been considered for both isomers and found to be nearly degenerate at this level, the I_h isomer being more stable by 0.10 eV. Besides, in the lower-spin states, Au_{13} distorts considerably from its original I_h-like structure, making the comparisons with C_5Au_{12} inadequate. The $C_{central}$–Au distances are close for both isomers of C_5Au_{12} (Table 1), being more uniform for the I_h isomer, and are longer by ≈ 0.2 Å than the $Au_{central}$–Au distances (2.86–2.87 and 2.88–2.98 Å for the I_h and O_h isomers of Au_{13}, respectively) due to a larger size of the C_5 core compared to the Au atom. The distances between the peripheral Au atoms are also generally larger in C_5Au_{12} than in Au_{13} (3.00–3.03 and 2.90–2.95 Å for the two respective Au_{13} isomers). For the O_h isomer of C_5Au_{12}, however, this does not apply to gold atoms from different CAu_3 groups.

The atomization energy of C_5Au_{12} is predicted to be 41.0 eV for both the I_h and O_h isomers, with the energy of dissociation into C_5 + 12 Au of 18.6 eV or on average ≈ 1.5 eV per gold atom. Here the C_5 radical has been optimized for a few spin states as well, with the triplet state found to be most stable (hence used as the asymptote), followed by the quintet state which is 1.42 eV higher in energy. The above energy for detachment of all gold atoms is close to the calculated atomization energy of 18.0 eV for Au_{13} in its sextet state.

Model interaction–decomposition and CAu_4. In order to analyze the contributions to the total interaction energy of C_5Au_{12} (relative to C_5 + 12 Au), one can consider a model which splits it into the carbon–gold and gold–gold components:

$$V(C_5Au_{12}) \approx V(C_5\text{–}Au_{12}) + V(Au_{12}) = \sum_{Au}[V(C_5\text{–}Au) + \sum_{Au'} V(Au\text{–}Au')]$$

Here we should keep in mind that the gold pair interactions are effective, describing the Au atoms which are not free but attached to carbons. So to use the diatomic Au_2 potentials for V(Au–Au′) directly, or to equate $V(Au_{12})$ to the energy of the (geometry-frozen) Au_{12} shell with C_5 removed, would be an excessive simplification.

The next approximation is to treat the C_5–Au interaction locally, *i.e.* assuming it to be dominated by a single C–Au term involving the peripheral C atom to which the Au atom is bonded directly (within the CAu_3 group). This allows parameterization of the interaction by applying the same model to a smaller cluster with a similar structure, such as CAu_4:

$$V(CAu_4) \approx \sum_{Au}[V(C\text{–}Au) + \sum_{Au'} V(Au\text{–}Au')].$$

Here we should again keep in mind that the C–Au interactions are those between Au and a C which is not free, as it has three other atoms attached to it. To take this into account, we could consider the {$CAu_4 \rightarrow CAu_3 + Au$} dissociation (while keeping CAu_3 frozen in its CAu_4-originated geometry) as representing such an interaction.

For consistency, calculations for CAu_4 and "frozen" CAu_3 have been carried out at the same level of theory, B3LYP/6-31G* (C) + LanL2DZ (Au), as for C_5Au_{12}. The CAu_4 molecule is found to be perfectly tetrahedral in its singlet ground state (Fig. 4), similar to the analogous $SiAu_4$ system.[12] The C–Au and Au–Au distances are 2.004 and 3.273 Å, respectively, close to the values for C_5Au_{12} (within the CAu_3 groups), which justifies using CAu_4 for the parameterization. The triplet state of CAu_4 is calculated to be 1.4 eV higher in energy. The CAu_3 radical doublet-state energy has been calculated for the optimized geometry of CAu_4, with one gold atom removed.

For the above geometry we can write the interaction energies of these species, within the same model:

$$V(CAu_4) \approx 4V(C\text{–}Au) + 6V(Au\text{–}Au)$$
$$V(CAu_3) \approx 3V(C\text{–}Au) + 3V(Au\text{–}Au).$$

The calculated atomization energy of CAu_4 (relative to C + 4Au) is 9.46 eV, or on average 2.36 eV per gold atom. From rearranging the above equations, we obtain

$$V(C\text{–}Au) \approx V(CAu_3) - V(CAu_4)/2 = -2.44 \text{ eV}$$
$$V(Au\text{–}Au) \approx V(CAu_4)/2 - 2V(CAu_3)/3 = 0.05 \text{ eV}.$$

So the DFT approach does not predict aurophilic interaction for this case, at least according to the model.

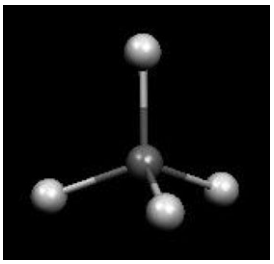

Fig. 4 Optimized geometry of CAu_4 (singlet).

The system is, however, sufficiently small to allow a more accurate calculation. Using MP2 with the same basis set, we obtain $V(CAu_4) = -10.43$ eV, which is 1 eV lower than the DFT result and close to the value of −10.87 eV for $SiAu_4$.[12] This leads to V(C–Au) = −1.82 eV and V(Au–Au) = −0.53 eV, thus predicting a significant aurophilic interaction contributing 30% to the total interaction in CAu_4. This Au–Au interaction is appreciable but much smaller compared to $D_e \approx$ 2 eV of the Au_2 dimer, as has been anticipated, while the C–Au interaction energy is close to that in the AuC diatom. Note that at the MP2 level, the C–Au interaction is reduced relative to DFT, so the sum of V(C–Au) and V(Au–Au) is almost the same for both DFT and MP2, and this is, consequently, true for $V(CAu_3)$. The MP2 C–Au and Au–Au distances in the still perfectly tetrahedral CAu_4 slightly shrink relative to their DFT values, to 1.984 and 3.239 Å, respectively. More detailed work on CAu_4, also including its other isomers, will be presented in a separate publication.

The calculated (DFT) energy of C_5Au_{12} relative to C_5 + 12 Au is −26.66 eV, for the representative case of the triplet O_h isomer (here C_5 has been frozen in its geometry inside the cluster, with the triplet and singlet states being almost degenerate). The difference of this energy from that (obtained above) for the optimized C_5 reflects a considerable variation in geometry between the isolated and embedded C_5. Making use of the similarity of the CAu_3 groups in C_5Au_{12} and in CAu_4, we can attempt the following estimate:

$$V(C_5Au_{12}) \approx 12V(C\text{–}Au) + V(Au_{12}),$$

so that $V(Au_{12}) \approx 2.62$ eV. DFT thus again predicts an aurophobic rather than aurophilic interaction, consistent with the CAu_4 case, and this interaction is stronger compared to that for the small system due to more Au–Au pairs being involved.

The MP2 level of theory is too computationally expensive to be applied to C_5Au_{12} directly and beyond the scope of the present work. This level can, however, be tried to be incorporated *via* the system fragments, by employing the above mentioned equivalence of the DFT and MP2 results for the CAu_3 groups. If we approximately adopt the V(Au–Au) value from CAu_4 as that within the CAu_3 groups of C_5Au_{12}, we could split the total gold–gold interaction in C_5Au_{12} into the contributions from within and between (V' below) the groups:

$$V(Au_{12}) \approx 12V(Au\text{–}Au) + \sum_{Au} V'(Au\text{–}Au),$$

hence

$$V(C_5Au_{12}) \approx 12V(C\text{–}Au) + 12V(Au\text{–}Au) + \sum_{Au} V'(Au\text{–}Au).$$

If the last term is relatively small (to be verified below), then $V(C_5Au_{12})$ is dominated by the intra-CAu_3 interactions and can be expected to have close values for DFT and MP2. When

using the DFT value for $V(C_5Au_{12})$ in combination with the MP2 values for V(C–Au) and V(Au–Au), the between-groups interactions add up to a repulsion: $\sum_{Au} V'(Au–Au) \approx 1.54$ eV, while the overall gold–gold interaction is attractive, $V(Au_{12}) \approx -4.82$ eV, and contributes 18% to $V(C_5Au_{12})$.

The repulsive component can be rationalized as being not completely due to the approximations made if to take into account the following. First, the Au–Au distances for the between-groups interactions are shorter than those within the CAu_3 groups (Table 1). In particular, when recalculated for reduced C–Au (and hence Au–Au) distances in CAu_4, V(Au–Au) does become significantly less attractive. Second, the relative orientations of the C–Au bonds (polarizing the Au atoms) for the between-groups and within-groups interactions are different, which may also affect the V'(Au–Au) value. Third, the CAu_3 groups are bond-saturated systems analogous to the CH_3 groups in organic molecules and could therefore produce a steric repulsion as well. In particular, the lower dissociation energy per gold atom in C_5Au_{12} compared to CAu_4 is consistent with such a steric repulsion. This issue will be addressed in more detail in further work.

Finally, the sum of the between-group interactions amounts to less than 6% of the total interaction energy, which validates the above estimate. Thus a value of around -5 eV could be reasonably expected for the gold–gold interactions in C_5Au_{12}, *i.e.* about 1/4 relative to the carbon–gold interactions (≈ -22 eV).

3.2 Cluster ions

3.2.1 $C_5Au_{12}^-$. Next, ionic derivatives of the neutral clusters are investigated. Addition of an electron to C_5Au_{12}, in particular in its I_h-shaped singlet state, and subsequent optimization have resulted in O_h-shaped structures of $C_5Au_{12}^-$. The electron attachment thus favours the O_h isomer, which is different from the I_h shapes predicted for MAu_{12}^-.[13] The doublet state of $C_5Au_{12}^-$ has the lowest energy, and the quartet and sextet states are higher by 0.61 and 1.20 eV, respectively. The adiabatic electron affinity (AEA) of the neutral cluster is found to be ≈ 2.8 eV (relative to the doublet ground state of the ion). Real vibrational frequencies confirm an energy minimum for the predicted structure, adding up to the zero-point energy of 0.68 eV.

The negative-ion geometry (visually identical to that in Fig. 3c), as compared to that for the neutral (O_h) cluster, is marked by a slight increase of the C–C distances and of their variation interval as well. On the other hand, no noticeable changes are seen in the C–Au distances except for their more even values (Table 1). Another difference is a narrowed variation interval of the Au–Au distances within the CAu_3 groups, but with no visible difference for such distances between the groups. These features are absent for the quartet state of the ion, exhibiting almost constant C–C distances and a wider variation in the same-carbon bonded Au–Au distances, similar to the neutral-cluster case.

The Mulliken populations indicate that the additional negative charge is localized almost entirely on the Au atoms. This is consistent, from an electrostatic viewpoint, with their positive charge in the neutral system as well as with the negatively charged carbon core pushing the additional negative charge outside. Another structural indication of such a charge distribution is the slightly increased Au–Au distances in the ion, in accord with a longer bond in Au_2^- compared to Au_2 (verified by present B3LYP/LanL2DZ calculations).

The above AEA ≈ 2.8 eV for C_5Au_{12} is significantly smaller than the value of ~ 3.8 eV for the sextet state of Au_{13}, calculated at the equivalent B3LYP/LanL2DZ level, relative to the quintet state of Au_{13}^-. By comparison, the MAu_{12} species have been determined[13] to have the adiabatic detachment energies (equivalents of AEA) close to that for Au_{13}. The reduction of AEA for C_5Au_{12} could be related, physically, to the negatively charged C_5 core as compared to the positively charged central atom in the gold cluster. The calculated high value for Au_{13}, exceeding that for a halogen atom and thus making the cluster (as well as MAu_{12}) another ''superhalogen'', agrees well with the previous DFT values of 3.7–3.9 eV for the fixed O_h symmetry.[14] It is worth noting that the I_h isomer of Au_{13} relaxes upon addition of an electron into the O_h isomer of Au_{13}^- (similar to the C_5Au_{12} case), consistent with the experiments ruling out the I_h geometry of the gold cluster ion.[15]

Consistent with the above, the vertical electron detachment (VDE) energies for the ground state $C_5Au_{12}^-$, are ≈ 2.9–3.0 eV for both singlet and triplet states of the resulting neutral, which is ~ 1 eV smaller than the value for the corresponding O_h isomer of Au_{13}^-. In addition, the vertical electron attachment (VEA) energy of the C_5Au_{12} is somewhat larger (by ~ 0.4 eV) for its O_h isomer relative to the I_h isomer (Table 2) for the doublet states of the ion, similar to the case of Au_{13}. For both C_5Au_{12} isomers the VEA values are, again, significantly lower (by 0.8–0.9 eV) compared to those for the gold cluster, while equally higher than the values of 2.1–2.2 eV for WAu_{12} and $MoAu_{12}$.[7] For formation of quartet $C_5Au_{12}^-$ from triplet C_5Au_{12} the VEA value of 2.1 eV is still smaller.

By comparison, the MAu_{12}^- systems generally do not show much of a reduction in the VDE/VEA values relative to Au_{13}^-,[13] except for the M = W and Mo cases. These cases have been interpreted in terms of the closed-shell electronic structure of the WAu_{12} ($MoAu_{12}$) cluster, with the additional electron in the ion opening a new shell. A similar

Table 2 Calculated vertical energies (in eV) of electron attachment (VEA) and ionization (VIE) of C_5Au_{12} and Au_{13}, and of electron detachment (VDE) of $C_5Au_{12}^-$ and Au_{13}^-. The values are arranged to correlate to the process products

		I_h	O_h
C_5Au_{12}	$S = 0$		VDE = 2.98
	$S = 1$		2.86[c]
$C_5Au_{12}^-$	$S = 1/2$	VEA = 2.33	VEA = 2.75/2.68[b]
	$S = 3/2$		2.09[b]
$C_5Au_{12}^+$	$S = 1/2$	VIE = 6.04	VIE = 6.15/6.18[b]
	$S = 3/2$		6.09[b]
Au_{13}	$S = 5/2$		VDE = 3.91
Au_{13}^-	$S = 2$	VEA = 3.11	VEA = 3.58
Au_{13}^+	$S = 2$	VIE = 6.76	VIE = 6.29

[a] The default multiplicities are singlet for C_5Au_{12} and doublet for $C_5Au_{12}^{\pm}$. [b] From triplet C_5Au_{12}. [c] From quartet $C_5Au_{12}^-$.

interpretation could be proposed for $C_5Au_{12}^-$ *via* considering it as a singlet (closed-shell) C_5Au_{12} with additional electron.

3.2.2 $C_5Au_{12}^+$. Removal of an electron from the singlet I_h and O_h isomers approximately preserves their overall shapes for the doublet states of $C_5Au_{12}^+$ (except for making the O_h structure more symmetric), with geometries resembling those in Fig. 3a and c. Both isomers have close adiabatic ionization energies (AIE) of 5.96 and 6.04 eV, respectively. For the quartet state of the ion, only an O_h-shaped final structure (indistinguishable from that in Fig. 3c) is produced, in particular when starting from the I_h geometry. It is slightly lower in energy relative to the doublet state (by $\approx$ 0.09 eV) and almost degenerate with the doublet I_h case. The ionization thus seems to keep the relative energy tie between the two isomers. The corresponding sextet state is found to be $\approx$ 0.8 eV higher in energy.

The vibrational frequencies for each of the respective lowest energy states (doublet for I_h and quartet for O_h) are real, confirming a minimum of energy. The zero-point energy amounts to 0.72 eV for both isomers.

The interatomic distances for the doublet I_h isomer of the ion are essentially the same as for the neutral cluster, except for the noticeably shorter distances between the nearest-neighbour Au atoms belonging to different CAu_3 groups (Table 1). The same applies, although to a lesser degree, to the doublet O_h isomer.

This would suggest a positive-charge concentration in the gold shell of $C_5Au_{12}^+$, as the distance between atoms is also slightly shorter (by 0.02 Å) in Au_2^+ as compared to Au_2, according to auxiliary B3LYP/LanL2DZ calculations. The Mulliken populations confirm the positive charge as being located almost entirely on the gold atoms for both isomers, similar to the above negative-charge case. This may be attributed to the energetically preferred location for the charge on the surface of the initially neutral system (which could apply to the $C_5Au_{12}^-$ case as well).

The interatomic distances for the (ground) quartet state of the O_h isomer are the same as for the doublet state, being invariable (within $\approx$ 0.002 Å) for a given pair of atom types: C–C, C–Au, and Au–Au within or between the CAu_3 groups (Table 1). This is different for the sextet state, for which the atom–atom distances vary significantly (up to 0.15 Å for the Au–Au pairs). The Mulliken charge distribution for the quartet state is the same as for the doublet O_h case.

The above AIE values of $\approx$ 6.0 eV for both C_5Au_{12} isomers are close to those for the corresponding Au_{13} cluster, namely $\approx$ 5.8 and 6.1 eV for its sextet I_h and O_h isomers, respectively. The latter values have been obtained from B3LYP/LanL2DZ calculations for Au_{13}^+ in its quintet state. This relatively small variation between C_5Au_{12} and Au_{13} is consistent, on electrostatic grounds, with considering their ionization as electrically charging similar gold surfaces of clusters of comparable sizes, even though their central parts are different (C_5 radical and Au atom).

The vertical ionization energies (VIE) are almost the same (6.1 $\pm$ 0.05 eV) for both I_h and O_h isomers of C_5Au_{12} (the latter case including $S = 0$ and 1 states of the neutral and $S = 1/2$ and 3/2 state of the ion). This value is close to that for the O_h isomer of Au_{13}, but somewhat lower than that for its I_h isomer (Table 2). The latter could be associated with a stronger ionization-induced variation of the Au_{13} geometry found to change from the original I_h-like one.

For a preliminary analysis of the dependence of the above results on the basis set used, single-point energy calculations have been carried out for the optimized geometries of the neutral cluster and its ions using the Stuttgart's ECP with an associated (larger) basis set for the Au atom. The main variation from the previous results is the overall relative stabilization of the O_h species, both neutral and ionic, relative to the I_h species, by around 0.5 eV. For the neutral cluster, the triplet (O_h) state remains marginally lower relative to the singlet (by 0.04 eV), the latter being 0.52 eV more stable than the I_h singlet. The EA value for the O_h isomer (relative to the negative-ion doublet) slightly decreases by $\sim$0.1 eV (to $\approx$ 2.7 eV). The AIE value remains the same within $\sim$0.1 eV (at $\approx$ 5.9 eV) for the singlet states of both isomers (relative to the positive-ion doublet), is lower by $\sim$0.2 eV for the O_h isomer triplet relative to the ion quartet, while the doublet–quartet splitting in the O_h ion increases somewhat (to 0.27 eV), with the quartet remaining lower in energy. A more detailed analysis of the basis set sensitivity of the results should involve geometry reoptimization with the larger basis set, which is beyond the scope of the present work.

4 Conclusions

The C_5Au_{12} cluster has been constructed and investigated (together with its positive and negative ions) at a DFT level of theory, for a few spin multiplicities for each system. Stable structures have been predicted, with the (tetrahedrally shaped) C_5 radical being a core encapsulated in the monoatomic gold layer of matching geometry, and with the Au atoms in positions correlating to the pattern of bonds of the sp^3-hybridized carbons.

Two groups of isomers have been characterized, the icosahedral-like (I_h) isomer and the octahedral-like (O_h) isomer, both related to similar isomers of the Au_{13} cluster as well as to the analogous C_5H_{12} molecule. The fully optimized geometries generally lack precise symmetry, with interatomic distances varying significantly due to a mismatching size of C_5, except for the highly symmetric structure of $C_5Au_{12}^+$. The two isomers are close in energy for the cases of C_5Au_{12} and $C_5Au_{12}^+$ in their lowest-spin states, while for their higher-spin states and for $C_5Au_{12}^-$ the O_h isomer prevails. This is consistent with the fact that the higher multiplicity or addition of negative charge reduces binding between the Au atoms (as in Au_2), and that the C_5H_{12} molecule (with no H–H bonding) is O_h-shaped. In addition, for the negative ion the octahedral shape is preferred by the pure gold cluster (and thus by its external layer which is also present in the carbon–gold cluster) as well. There is, however, an indication that with increasing basis set the relative stability of the lowest-spin state O_h isomer may also increase, which is an issue to be addressed in further work.

The ground states are found to be triplet (nearly degenerate with singlet) for C_5Au_{12}, doublet for $C_5Au_{12}^-$ and quartet (close in energy to doublet) for $C_5Au_{12}^+$. The octahedral shape

of these species, promoted by the C_5 core, is different from the icosahedral geometry of metal-doped MAu_{12} and MAu_{12}^-.

A simple model is developed for separating the carbon–gold and gold–gold components of the total interaction by means of a fragment-based approach employing the structural similarity of the CAu_3 groups in C_5Au_{12} and CAu_4. This allows a higher level of calculation (MP2 in this work), achievable for the small system, to be incorporated into the larger cluster. Within the model, the overall interaction in the gold layer of C_5Au_{12} is predicted to be attractive (aurophilic) and to contribute about 20% into the total interaction energy (relative to $C_5 + 12Au$). This total interaction is found to be dominated by the C–Au and Au–Au interactions within the CAu_3 groups and to be somewhat reduced by a steric repulsion between the groups.

The C_5 core of C_5Au_{12} is found to be negatively charged and the Au_{12} layer positively charged, which is different from the negatively charged surfaces of the Au_{13} (and WAu_{12}) clusters and reflects the higher electronegativity of carbon. For $C_5Au_{12}^{\pm}$ the extra charge is predicted to be localized on the surface, consistent with the system structure resembling, at molecular level, an insulating centre covered with a metal film.

The electron affinities (adiabatic and vertical) of C_5Au_{12} are significantly lower than those of Au_{13} (as well as MAu_{12}). The adiabatic and vertical ionization energies, however, show much smaller differences between the two systems. ''Doping'' of the gold cluster with the carbon radical thus makes the cluster less electronegative (more metallic), weakening it as an electron acceptor while keeping it as donor, *i.e.* affecting the properties selectively. This shows a potential for tuning catalysts in a desired direction.

The clusters studied belong to a family of molecule- (or radical-) doped metal clusters, with other representatives being the subject of future work. The above variations in electron-donating and -accepting parameters illustrate possible modifications of catalytic and other chemical properties of such systems. Another possible application concerns the possibility of mechanical strengthening of metal clusters *via* incorporating molecular-level ''diamond'' centres. These properties are being investigated as well. Such clusters can be considered as potential building blocks for creating new (and in particular cluster-assembled) materials with unique properties, potentially including diamond-hard metal composites.

The predicted high stability of the C_5Au_{12} cluster relative to atomization and dissociation into $C_5 + 12$ Au would favor its formation, perhaps in a mixture of laser-evaporated carbon and gold, or by means of another established cluster-generating technique. The efficiency of producing the desired structure under such conditions is, however, an open issue. Solution chemistry should not be ruled out either as a promising alternative method. It would be interesting and most likely challenging to produce such a system and analyze its properties experimentally.

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