Electron count and electronic structure of bare icosahedral Au₃₂ and Au₃₃ ionic nanoclusters and ligated derivatives. Stable models with intermediate superatomic shell filling†

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DFT calculations were carried out on bare Au₃₂ and Au₃₃ nanoclusters with various charges, in order to analyze their stability with respect to different cluster electron numbers. Results indicate that in addition to the neutral Au₃₂ hollow species, significant HOMO-LUMO gaps are computed for [Au₃₂]⁸⁺ (hollow) and [Au₃₂]⁴⁺ (two-shell structure). Species with smaller HOMO-LUMO gaps can reach stability upon “passivation” by a ligand shell, as experimentally exemplified. Icosahedral frameworks of *I_h* or lower symmetry are favored for the cationic nanoclusters whereas different structures are computed for the anionic ones.

Introduction

Gold clusters have attracted increased interest due to their size-dependent characteristics making them useful templates for nanosized species, for further applications in several fields ranging from catalysis, nanoelectronics, among others.¹ In 2004, Johansson *et al.*² and Gu *et al.*³ predicted simultaneously the thermal stability of the bare neutral golden hollow cluster Au₃₂, the structure of which adopts a fullerene-type geometry of *I_h* symmetry (the so-called *golden-fullerene cage*). Although there is no direct experimental determination of its structure so far – only photoelectron spectroscopy (PES) experiments were carried out⁴ – it is likely to be one of the very lowest energy minima of bare Au₃₂, although the structure of its true ground state remains controversial.⁵ This is a spherical deltahedral arrangement describing a regular 32-vertex–60-face pentakis dodecahedron, a Catalan solid which is the dual polyhedron of the truncated icosahedron (the framework of C₆₀). Such a polyhedron displays two types of symmetry-equivalent vertices, divided in a group of 12 equivalent vertices Au_{ico} describing an icosahedron and a group of 20 equivalent Au_{dod} vertices describing a regular dodecahedron. The latter polyhedron, which exhibits 12 pentagonal faces, is the dual polyhedron of the icosahedron (top of Figure 1). Thus, the Au₃₂ cluster can be described as made of two nested polyhedra (Au₁₂ and Au₂₀) of approximately equal center-to-vertex radius. In this pseudo-spherical arrangement, there are Au_{dod}–Au_{dod} and Au_{dod}–Au_{ico} contacts, but no Au_{ico}–Au_{ico} contacts.

Figure 1. Top: The one-shell neutral Au₃₂ hollow cluster, as theoretically predicted.^{2,3} The nested Au₁₂ icosahedron and Au₂₀ dodecahedron are shown in blue and orange, respectively. Bottom: The 2-shell Au₁₂@Au₂₀ core, as found in Au₃₂Cl₈(PR₃)₁₂ (R = Et, ⁿPr, ⁿBu)¹⁴ and [Au₃₂(PPh₃)₈(dpa)₆]²⁺ (Hdpa = 2,2'-bipyridylamine).¹⁵

The stability of Au₃₂ supported by a few theoretical studies^{6,7} is related to its valence cluster electron number (*cen*), i.e., 32 – 5d electrons are not considered – which provides the cluster with shell closure and spherical aromaticity. This electron count is in line with Mingos' electron counting rules for hollow spherical clusters in which the bonding is predominantly ensured by σ-type (radial-type) orbitals, gold 6s AOs in the present case.^{8,9} The model on which are based these rules is that of nearly free electrons constrained to move on the surface of a sphere of a given radius. Within this

†Electronic Supplementary Information (ESI) available: Simulated UV-vis spectra and Cartesian coordinates in .xyz format.

model, the solutions of the Schrödinger equation are simply the spherical harmonics expressed with respect to an origin situated at the center of the cluster sphere. For 32 electrons, the corresponding closed-shell configuration is $S^2 P^6 D^{10} F^{14}$.

It is noteworthy that this *cen* is not a *superatom* “magic” number.¹⁰⁻¹³ Indeed, *superatoms* are not only spherical, but also close-packed (non-hollow) clusters, or at least multi-shell (onion-like) systems. Their electron counting rules are based on the spherical *jellium* model, which is related to that of nearly free electrons constrained to move *inside* a sphere. The nearest *superatom* closed-shell (“magic”) number is 34, i.e., $1S^2 1P^6 1D^{10} 2S^2 1F^{14}$. Thus, from the 32-*cen* hollow system to a 34-*cen* non-hollow one, the difference lies in the occupied 2S level in the latter that does not exist in the former (which is a single pseudo-spherical shell).

One should also take into account that the F-type orbitals, which are degenerate in the ideal R_3 symmetry of the sphere, split into two levels, namely t_{2u} and g_u , in I_h symmetry. Thus, the possibility for closed-shell electron counts with partial filling of the F shell, namely 24 ($t_{2u}^6 g_u^0$) or 26 ($g_u^8 t_{2u}^0$) should not be excluded. These alternative potentially favor electron counts with such partial F-shell fillings would correspond to $[Au_{32}]^{8+}$ and $[Au_{32}]^{6+}$, respectively, of which the large cationic charge could be counterbalanced by the presence of a peripheral shell of formally anionic ligands. It turns out that in 2019, two strongly related species of 24-*cen* ligated Au_{32} nanoclusters were simultaneously published by the groups of Schnepf¹⁴ and Wang,¹⁵ namely $Au_{32}Cl_8(PR_3)_{12}$ ($R = Et, ^nPr, ^nBu$)¹⁴ and $[Au_{32}(PPh_3)_8(dpa)_6]^{2+}$ ($Hdpa = 2,2'$ -bipyridylamine), respectively. These clusters have similar structures with an icosahedral metal kernel that can be described as an inner Au_{12} icosahedron encapsulated within an outer Au_{20} dodecahedron ($Au_{12}@Au_{20}$). Thus, unlike the bare neutral one-shell Au_{32} cluster predicted by Johansson *et al.*² and Gu *et al.*,³ where the two nested Au_{12} and Au_{20} polyhedra have roughly the same radius, the 24-electron $[Au_{32}]^{8+}$ core of the Schnepf’s¹⁴ and Wang’s¹⁵ clusters exhibits a two-shell onion-like structure, with a shrunk Au_{12} icosahedron lying inside an enlarged Au_{20} dodecahedron (bottom of Figure 1). The 2S shell is thus expected to be occupied, leading to the $1S^2 1P^6 1D^{10} 2S^2 1F^4$ closed-shell configuration claimed by Schnepf and collaborators.¹⁴ The I_h -forbidden splitting of the 1F level (two occupied orbitals below five vacant orbitals) is rationalized from the (moderate) distortion of the metal core from I_h to S_6 symmetry. On the other hand, the MO analysis provided by Wang and collaborators¹⁵ is rather consistent with the $1S^2 1P^6 1D^{10} 2S^0 1F^6$ closed-shell configuration, indicating that the electron configuration of the $[Au_{32}]^{8+}$ kernel may be ligand-controlled. The six 1F electrons occupying the expected t_{2u} component in I_h symmetry, the effect of lowering to S_6 symmetry is only to increase the HOMO-LUMO gap.

In this paper, we investigate the possibility of stabilizing an icosahedral Au_{32} architecture with seven potential closed-shell electron counts, corresponding to partial filling of the 1F shell, but also for possible filling of the 2S orbital, owing to the fact that a two-shell onion-like structure could be sufficiently compact for behaving as a *superatom* with a filled 2S orbital. The ten following tentative closed-shell configurations are summarized in Table 1. It

turns out that while we were writing this paper, an elegant theoretical work by Lin and collaborators on bare and ligated compounds containing the $[Au_{32}]^{8+}$ and $[Au_{32}]^{4+}$ kernel came out.¹⁶ Our results on these two particular electron counts are in large part similar to theirs (see

Table 1. The various $1S^2 1P^6 1D^{10} 2S^x 1F^y$ closed-shell electron configurations investigated for different bare icosahedral $[Au_{32}]^q$ architectures.

Expected structure	Expected electron configuration $2S^x 1F^y$		<i>cen</i> = 18 + x + y	Cluster charge (q)	Computed results		
	x	y			Optimized structure	HOMO-LUMO gap (eV)	Remark
One shell	0	0	18	+14	-	-	Unbound structure
One shell	0	6	24	+8	One shell	1.13	I_h
One shell	0	8	26	+6	$Au_{12}@Au_{20}$ (see below)	0.35	C_2 -distorted (see below)
One shell	0	14	32	0	One shell	1.55	I_h
$Au_{12}@Au_{20}$	2	0	20	+12	$Au_{12}@Au_{20}$	0.20	I_h
$Au_{12}@Au_{20}$	2	4	24	+8	$Au_{12}@Au_{20}$	0.27	D_{2d}
$Au_{12}@Au_{20}$	2	4	24	+8	$Au_{12}@Au_{20}$	0.33	C_2 -distorted with $2S^0 1F^6$ configuration
$Au_{12}@Au_{20}$	2	6	26	+6	$Au_{12}@Au_{20}$	0.35	C_2 -distorted with $2S^0 1F^8$ configuration
$Au_{12}@Au_{20}$	2	8	28	+4	$Au_{12}@Au_{20}$	0.99	C_2 -distorted
$Au_{12}@Au_{20}$	2	14	34	-2	Non-icosahedral structure	0.93	Encapsulated triangle $Au_3@Au_{29} (C_1)$

Table 2. The various $1S^2 1P^6 1D^{10} 2S^x 1F^y$ closed-shell electron configurations investigated for bare icosahedral atom-centered $[Au_{33}]^q$ architectures.

Expected structure	$1F^y$		<i>cen</i> = 20 + y	Cluster charge (q)	Computed results		
	x	y			Optimized structure	HOMO-LUMO gap (eV)	Remark
$Au@Au_{12}@Au_{20}$	0	20	+13	+13	$Au@Au_{12}@Au_{20}$	0.26	I_h
$Au@Au_{12}@Au_{20}$	6	26	+7	+7	$Au@Au_{12}@Au_{20}$	0.27	C_2 -distorted
$Au@Au_{12}@Au_{20}$	8	28	+5	+5	$Au@Au_{12}@Au_{20}$	0.86	C_2 -distorted
$Au@Au_{12}@Au_{20}$	14	34	-1	-1	Non-icosahedral structure	1.08	Encapsulated triangle $Au_3@Au_{30} (C_1)$

below). The possibility to add a supplementary Au atom at the cluster center is also investigated. Such a situation is expected to favor the occupation of the 2S orbital, thus suggesting the possible closed-shell configurations given in Table 2. Indeed the icosahedral $X@Y_{12}@Z_{20}$ matryoshka arrangement is well documented in cluster chemistry.¹⁷⁻¹⁹

Computational details

Geometry optimizations and subsequent calculations were performed on bare and ligated Au_{32} and Au_{33} clusters at the Density Functional Theory (DFT) level,²⁰ with the Amsterdam Density Functional (ADF) code,^{21,22} employing the Becke-Perdew (BP86) exchange-correlation functional within the generalized gradient approximation (GGA),^{23,24} and the valence triple zeta basis set, plus 2 polarization function (TZ2P).²⁵ The relativistic effects were treated at the scalar level by using the Zeroth Order Regular Approximation (ZORA) Hamiltonian.²⁶ Empirical Grimme DFT-D3 corrections were included to account for dispersion forces.²⁷ Vibrational frequency

analysis was performed to check that the optimized geometries were minima on their potential energy. Clusters models with large positive charges (see Table 1) were computed both as isolated species in vacuum and in solution using the dielectric Conductor like Screening Model (COSMO) of solvation.²⁸ The solvent (dichloromethane and dimethylformamide) effects were supposed to take into account, at least partly, the effects of the counter-anion.²⁹ It turns out that, for all the computed cations, calculations both in vacuum and solvent provided similar results. Thus, calculations taking into account solvent effects are not further discussed below. Fragment decomposition analyses were carried out by single-point calculations using the optimized geometries. Time-dependent density functional theory (TD-DFT) calculations³⁰ were performed with the Gaussian 16 package³¹ (chosen for CPU time efficiency) using the hybrid B3LYP functional³² and the split valence Def2-TZVP basis set.³³ As suggested by a reviewer, the long-range corrected CAM-B3LYP functional³⁴ was also tested (Figure S3). It provided results in a less satisfying agreement with the experimental spectrum of $\text{Au}_{32}\text{Cl}_8(\text{PR}_3)_{12}$ ¹⁴ than with B3LYP.

Results and discussion

Relevant computed results corresponding to the various computed configurations of bare $[\text{Au}_{32}]^q$ models are gathered in Table 1. Their optimized structures are shown in Figure 2 and metrical data are given in Table 3. Ground-state closed-shell configurations were found for all the computed systems, except for the $[\text{Au}_{32}]^{14+}$ model ($cen = 18$), which yielded a dissociated structure, presumably because of its large cationic charge. Including solvent effects in the calculations provided similar results. As expected, the neutral $[\text{Au}_{32}]$ ($cen = 32$) one-shell hollow cluster of I_h symmetry exhibits the largest HOMO-LUMO gap among all the computed systems, in agreement with the prediction of Johansson and of Gu.²⁻⁴ Incidentally, this structure was found slightly distorted to D_{2h} in a recent DFT investigation.^{5c} Substantial HOMO-LUMO gaps are also found for the one-shell $[\text{Au}_{32}]^{8+}$ ($cen = 24$), $[\text{Au}_{32}]^{4+}$ ($cen = 28$) and $[\text{Au}_{32}]^{2+}$ ($cen = 34$) clusters, indicating particular chemical stability for these electron counts. Both one-shell $[\text{Au}_{32}]^{8+}$ and $[\text{Au}_{32}]^{4+}$ systems are of icosahedral parentage,¹⁶ although the symmetry

of $[\text{Au}_{32}]$ and $[\text{Au}_{32}]^{4+}$ are shown in Figure 3, and that of the one-shell $[\text{Au}_{32}]^{8+}$ on the left hand-side of Figure 4.

Figure 2. Optimized geometries of the computed bare $[\text{Au}_{32}]^q$ models.

Table 3. Au-Au distances (Å) of the bare $[\text{Au}_{32}]^q$ clusters of icosahedral parentage. Average and range values are given for non- I_h symmetry.

Figure 3. Frontier orbital diagrams of $[\text{Au}_{32}]$ (left) and $[\text{Au}_{32}]^{4+}$ (right). Only 1F and 2S Kohn-Sham orbitals are plotted.

obtained for our optimized geometry of $[\text{Au}_{32}]^{4+}$ is lowered to C_i . Its major feature is a lengthening of six among the 30 edges of the Au_{20} dodecahedron (3.84 Å vs. 3.15 Å avg.). The frontier orbital diagrams

The geometry optimization of the $[\text{Au}_{32}]^{2-}$ cluster provided an unexpected non-icosahedral structure of C_1 symmetry exhibiting an approximately equilateral Au_3 triangle (Au-Au avg. = 2.66 Å) encapsulated in an oblate Au_{29} envelope (Figure 2). Its significant HOMO-LUMO gap lets expecting potential stability for this structure. The non-stability of the icosahedral (pseudo-spherical) structure for this 34- cen count can be tentatively explained from the fact that more than half of the cluster 6s combinations, mainly responsible for cluster bonding, are filled, thus implying occupation of antibonding orbital(s) and favoring a structure with less connectivity and lower symmetry.

Among the considered electron counts for which a lower HOMO-LUMO gap was obtained, two of them, namely that of $[\text{Au}_{32}]^{6+}$ and $[\text{Au}_{32}]^{8+}$ deserve some comments. Independently from its starting geometry, the former converged to a unique structure corresponding to the $2S^0 1F^8$ configuration that is best described as

$\text{Au}_{12}@\text{Au}_{20}$ rather than the expected one-shell arrangement, although some of the Au-Au distances within the Au_{12} icosahedron are fairly large (3.07 Å). It is also distorted away from I_h to C_i symmetry (but close to T_h), presumably due to second-order Jahn-Teller instability in relation with its small HOMO-LUMO gap (0.35 eV).

The $[\text{Au}_{32}]^{8+}$ case is more striking. As said above, an I_h one-shell structure with the $2S^0 1F^6$ configuration and a large HOMO-LUMO gap was found for this species (Table 1). At first sight, an $\text{Au}_{12}@\text{Au}_{20}$ two-shell structure appears unfavorable for this 24-*cen* count since it would likely lead to the $2S^2 1F^4$ configuration, *i.e.*, to partial filling of one of the t_{2u} or g_u levels of 1F parentage.¹⁶ However, as mentioned earlier, diamagnetic ligated clusters with an $[\text{Au}_{32}]^{8+}$ kernel were experimentally characterized, exhibiting the $\text{Au}_{12}@\text{Au}_{20}$ two-shell arrangement.^{14,15} The solid state structure of these clusters departs from ideal I_h to approximate S_6 symmetry, a feature which was interpreted by Schnepf and collaborators¹⁴ as a Jahn-Teller effect allowing the stabilization of two of the 1F orbitals and the possibility of the $2S^2 1F^4$ closed-shell configuration. We thus looked for this putative configuration for a two-shell $[\text{Au}_{32}]^{8+}$ structure and found a minimum of D_{5d} symmetry in which the four 1F electrons occupy an e_{1u} level, all the other 1F levels are vacant (Figure 4). The rather small HOMO-LUMO gap (0.27 eV) obtained suggested possible HOMO-LUMO level crossings (thus electron configuration changes) upon moderate structural variations. As a matter of fact, when the starting structure used for the geometry optimization is an S_6 arrangement derived from the Au_{32} kernel present in the X-ray structure of the 24-*cen* $\text{Au}_{32}\text{Cl}_8(\text{PET}_3)_{12}$ nanocluster,¹⁴ then the closed-shell $2S^0 1F^6$ configuration was found instead (Figure 4). It is noteworthy that the corresponding optimized structure of exact C_i symmetry departs significantly from S_6 . It is only 0.08 eV more stable than the D_{5d} structure and surprisingly 0.55 eV more stable than the one-shell icosahedral

structure, despite its small HOMO-LUMO gap (0.33 eV).

Figure 4. Frontier orbital diagrams of the structures corresponding to the three minima computed for bare $[\text{Au}_{32}]^{8+}$: one-shell I_h (left), two-shell D_{5d} (middle), and two-shell C_i (right). Only 1F and 2S Kohn-Sham orbitals are plotted.

This result led us to wonder about the electronic structure of the Schnepf's¹⁴ and Wang's¹⁵ ligated clusters, as compared to bare $[\text{Au}_{32}]^{8+}$. The ligated $\text{Au}_{32}\text{Cl}_8(\text{PH}_3)_{12}$ cluster model was then computed to mimic Schnepf's systems $\text{Au}_{32}\text{Cl}_8(\text{PR}_3)_{12}$ ($R = \text{Et}, ^n\text{Pr}, ^n\text{Bu}$).¹⁴ As for bare $[\text{Au}_{32}]^{8+}$, its C_i optimized structure cannot be approximated to S_6 . Its Kohn-Sham orbital diagram is shown in Figure 5. It is consistent with that of the C_i two-shell $[\text{Au}_{32}]^{8+}$ model and thus to the $2S^0 1F^6$ configuration in contrary with the $2S^2 1F^4$ closed-shell configuration proposed by Schnepf.¹⁴ Interestingly, its HOMO-LUMO gap (0.87 eV) is larger than that of its isoelectronic bare metallic relative (0.33 eV). This finding suggests that bare $[\text{Au}_{32}]^9$ models with rather small HOMO-LUMO gaps can get supplementary chemical stability by interaction with a specific ligand sphere. Our results on $\text{Au}_{32}\text{Cl}_8(\text{PH}_3)_{12}$ are in turn consistent with previous calculations by Lin and colls. on the 24-*cen* $[\text{Au}_{32}(\text{PPh}_3)_8(\text{dpa})_6]^{2+}$ cluster.^{15,16}

As a supplementary proof for our computed electronic structure, we performed TD-DFT calculations on $\text{Au}_{32}\text{Cl}_8(\text{PH}_3)_{12}$ to simulate the UV-Vis spectrum of $\text{Au}_{32}\text{Cl}_8(\text{PR}_3)_{12}$ ($R = \text{Et}, ^n\text{Pr}, ^n\text{Bu}$).¹⁴ The simulated spectrum (Figure 6) shows a good agreement with the experiment.¹⁴ The intense high-energy band computed at 449 nm (exp. 480 nm)¹⁴ mostly involves $5d \rightarrow 1G$ electronic transition. The wide low-energy band is made of two major components at 620 and 685 nm (exp. 662 and 727 nm)¹⁴ mainly due to $1F \rightarrow 1G$ and $1F \rightarrow 1F$ electronic transitions, respectively. Similar calculations on the bare C_i $[\text{Au}_{32}]^{8+}$ species led to a similar shape of the simulated UV-Vis spectrum somewhat red-shifted (Figure 6). The computed spectra of the two other $[\text{Au}_{32}]^{8+}$ cores (I_h and D_{5d}) are also reported in Figure 6. Although the I_h structure exhibits a $5d \rightarrow 1G$ band at a similar energy than its C_i relative, the shape of its absorption curve is different higher energies. This result suggests that the simulated UV-Vis spectrum of the bare metal core ion should contain the

optical signature of its real ligand-protected counterpart. For this reason, we also performed TD-DFT calculations on all the other

models listed in Table 1 and gathered their simulated spectra in Figure S1.

Figure 5. Frontier orbital diagram of the $\text{Au}_{32}\text{Cl}_8(\text{PH}_3)_{12}$ model. Only 1F and 2S Kohn-Sham orbitals are plotted.

Figure 6. Simulated UV-Vis spectra of $\text{Au}_{32}\text{Cl}_8(\text{PH}_3)_{12}$ and of the various computed $[\text{Au}_{32}]^{8+}$ structures.

Pertinent results corresponding to some tested configurations of the atom-centered Matryoshka $[\text{Au}_{33}]^q$ model are gathered in Table 2. Their optimized structures are shown in Figure 7 and their metrical data are given in Table 4. Their TD-DFT-simulated UV-Vis spectra are shown in Figure S2, together with their non-centered isoelectronic relatives, for comparison. The frontier orbital diagrams of the three cationic species are plotted in Figure 8. Small HOMO-LUMO gaps are found for bare $[\text{Au}_{33}]^{13+}$ and $[\text{Au}_{33}]^{7+}$ (0.26 and 0.27 eV, respectively). Compared to the larger HOMO-LUMO gap computed for $[\text{Au}_{33}]^{5+}$ (0.86 eV), that of $[\text{Au}_{33}]^{7+}$ indicates that the preferential 1F splitting in the atom-centered (non-hollow I_h Au_{33} structure) is now four-below-three rather than three-below-four, leading to a $2\text{S}^2 1\text{F}^6$ closed-shell configuration. $[\text{Au}_{33}]^{5+}$ ($\text{cen} = 28$) and $[\text{Au}_{33}]^-$ ($\text{cen} = 34$) are likely to be stable, the first one when protected by an anionic ligand shell and the last one very likely as a bare anion. Interestingly, this anion has a non-icosahedral structure related to that of its $[\text{Au}_{32}]^{2-}$ isoelectronic relative, *i.e.*, an Au_3 triangle (Au-Au avg. = 2.66 Å) encapsulated in an Au_{30} oblate envelope (Figure 7). Moreover, the evaluated stability of $[\text{Au}_{32}]^{2-}$ and $[\text{Au}_{33}]^-$ kernels, suggests the plausible formation of ligand-protected clusters with charge states close to neutrality stabilized by neutral ligands like phosphines, or N-heterocyclic carbenes (NHCs), among others.

Table 4. Au-Au distances (Å) of the atom-centered $[\text{Au}_{33}]^q$ clusters of icosahedral parentage. Average and range values are given for non- I_h symmetry.

Figure 7. Optimized geometries of the computed $[\text{Au}_{33}]^q$ models.

Figure 8. Frontier orbital diagrams of the $[\text{Au}_{33}]^q$ cations of icosahedral parentage: $[\text{Au}_{33}]^{13+}$ (left), $[\text{Au}_{33}]^{7+}$ (middle), and $[\text{Au}_{33}]^{5+}$ (right). Only 1F and 2S Kohn-Sham orbitals are plotted.

Conclusions

DFT calculations carried out on various bare Au_{32} nanoclusters with various charges indicated that the hollow icosahedral arrangement is possible not only for the cluster electron number of 32 as initially predicted, but also for lower cluster electron numbers. In particular, when compared to their neutral $[\text{Au}_{32}]$ reference,^{2,3} the significant HOMO-LUMO gaps obtained for $[\text{Au}_{32}]^{8+}$ (one-shell) and $[\text{Au}_{32}]^{4+}$ (two-shell) led us to think that these architectures should also exhibit chemical stability, once protected by specific anionic ligand shells. Moreover, even with rather small HOMO-LUMO gaps, Au_{32} cations can reach stability when “passivated” by a ligand shell, as exemplified by the $[\text{Au}_{32}]^{8+}$ (two-shell) cation, stabilized as ligated species,^{14,15} with the same metal electron configuration ($2\text{S}^0 1\text{F}^6$). As several of our computed icosahedral models, this cation exhibits a distorted icosahedral arrangement. We suggest that this (possibly distorted) icosahedral structure is disfavored for electron counts larger than 32, as exemplified by the $[\text{Au}_{32}]^{2-}$ anion which exhibits an $\text{Au}_3@ \text{Au}_{29}$ flattened

structure. Interestingly, almost the same structure is obtained for the isoelectronic atom-centered $[\text{Au}_{33}]^-$ anion. Stability is expected for these two non-icosahedral structures, which suggests the possibility to stabilize them with neutral ligands. It should be noted that previous calculations on $[\text{Au}_{33}]^-$ found a similar structure as one of its low-energy minima.^{35,36} As we are interested in icosahedral structures we did not explore the whole energy surface of $[\text{Au}_{33}]^-$. In any case, a fragment decomposition analysis as provided by the ADF program²² allowed us to describe $[\text{Au}_{32}]^{2-}$ and $[\text{Au}_{33}]^-$ as consisting of a 2-electron $[\text{Au}_3]^+$ triangle encapsulated within 32-electron $[\text{Au}_{29}]^{3-}$ and $[\text{Au}_{30}]^{2-}$ envelopes, respectively. Both $[\text{Au}_3]^+$ and its host cage were found to exhibit significant HOMO-LUMO gaps as isolated fragments. Incidentally, the triangular $[\text{Au}_3]^+$ cation is isolobal to H_3^+ . Among the tested atom-centered icosahedral systems, the $[\text{Au}_{33}]^{5+}$ species has the largest HOMO-LUMO gap and is likely to be observed in the future. This 28-*cen* count appears to be favored for both hollow and atom-centered arrangements.

Conflicts of interest

There are no conflicts to declare.

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