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Icosahedral Au_{72}: a predicted chiral and spherically aromatic golden fullerene†

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Quantum chemical calculations demonstrate the spherical aromaticity and high thermodynamic stability of Au_{72}, a predicted *I*-symmetric golden fullerene.

Following the discovery of the C_{60} fullerene,[1] a few elements other than carbon, namely boron,[2a] phosphorus,[2b] and gold,[3] have been reported to be capable of forming hollow elemental cages. The special properties of gold, the only metal known to form hollow cages, can be traced to relativistic effects[4,5] and metallophilic attractions.[5] Besides the unusual structural characteristics, gold clusters have become particularly attractive due to their diverse catalytic applications.[6] Concerning hollow gold cages, systems with 16–18 atoms have been experimentally observed,[3] and larger ones, such as the icosahedral Au_{32},[7] theoretically predicted. Here we point out the possible existence of Au_{72}, a hollow nanosphere of gold exhibiting exceptional icosahedral chirality. Being strongly stabilised by spherical aromaticity,[8] the *I*-symmetric Au_{72} is shown to be thermodynamically favoured over the previously reported gold cages in Fig. 1, including the experimentally observed Au_{18}[3] and the tetrahedral Au_{20}.[9]

Anionic gold clusters up to about 11–13 atoms are flat (2D),[10] above which three-dimensional structures are preferred.[3] Considering neutral gold clusters, the preference for a tetrahedral pyramidal shape of the experimentally observed Au_{20}[9] can be rationalised by considering that 20 is a magic number of electrons for tetrahedral clusters, stabilising the tetrahedral shape by both electronic and atomic shell structure.[11] An icosahedral Au_{32} cage fulfilling the $2(N + 1)^2$ criterion of spherical aromaticity ($N = 3$) has been predicted to be energetically favourable over Au_{20}.[7] The space-filling isomers of Au_{32} were later found to surpass the hollow icosahedral cage in thermodynamic stability at temperatures above approximately 300 K.[12] The next icosahedral gold cage in size is Au_{42},[13] the existence of which has been theoretically predicted. Unlike Au_{32}, the Au_{42} cage is not spherically aromatic, resulting in lower stability and a significantly smaller HOMO–LUMO gap (Table 1). The recently predicted D_{6d}-symmetric Au_{50} cage,[14,15] in turn, obeys the $2(N + 1)^2$ rule ($N = 4$). The highest thermodynamic stability of Au_{50} amongst the previously reported hollow cages further emphasizes the stabilising effect of spherical aromaticity (Table 1).

Structural characteristics of hollow gold cages larger than Au_{50} are not well understood. Focusing on neutral gold clusters, the next cage in size fulfilling the criterion of spherical aromaticity, $2(N + 1)^2$ where ($N = 5$), is Au_{72}. The building principles of a 72-atom gold cage can be rationalised by considering the series of icosahedral cages as being composed of combined polyhedra. The first member of the icosahedral series is the Au_{12} icosahedron. While it is not a closed-shell system, and unstable as such, it can be synthesized in the presence of an endo-atom like W.[16] The next member of the icosahedral series is Au_{32}, whose structure can be derived by combining an icosahedron with a dodecahedron. Correspondingly, the icosahedral Au_{42} is a combination of an icosahedron and an icosidodecahedron. In analogy to the building

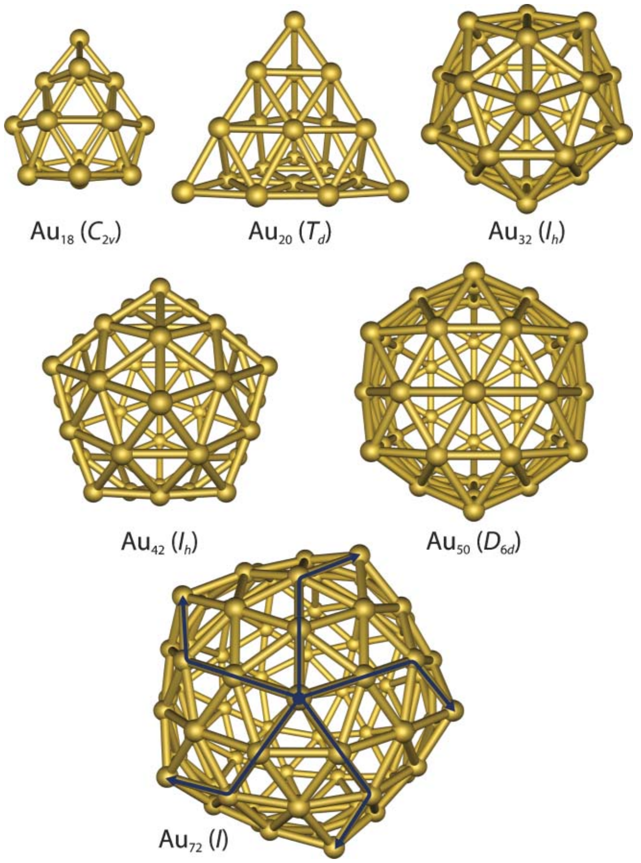

Fig. 1 Optimised structures of the studied gold cages. The chirality of Au_{72} is illustrated by lines between the centres of the neighbouring five-membered rings.

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Table 1 Relative total energies and Gibbs free energies (T = 298 K),[a] HOMO–LUMO gaps, NICS values, and diameters of the studied gold cages[b]

	ΔE_{BP86}	ΔG_{BP86}	ΔE_{MP2}	Gap/ eV	NICS (ppm)	Diameter/ nm
Au_{18} (C_{2v})	6.2	5.8	3.5	1.08	−45.4	0.7
Au_{20} (T_d)	0.0	0.0	0.0	1.91	−16.7	0.8
Au_{32} (I_h)	−10.8	−8.8	−28.4	1.60	−76.7	0.9
Au_{42} (I_h)	−10.6	−8.4	−24.9	0.42	125	1.0
Au_{50} (D_{6d})	−18.6	−15.8	−41.2	1.15	−88.5	1.1
Au_{72} (I)	−23.4	−20.1	−51.3[c]	0.72	−111	1.4

[a] The energies in kJ mol^{-1} per gold atom are given relative to the largest experimentally characterized gold cage, Au_{20}. [b] Gaps, diameters, and Nucleus-independent Chemical Shift (NICS) values[19] at the centre of the cage obtained from BP86/def2-TZVP calculations. [c] MP2/def2-TZVP single point calculation at the BP86-optimised geometry.

principles of Au_{12}, Au_{32} and Au_{42}, we derived the next member of the icosahedral series by combining an icosahedron with a snub dodecahedron. The outcome was Au_{72}, a spherically aromatic, chiral, I-symmetric cage (Fig. 2).

Besides the structural description by means of combined polyhedra, an alternative way to rationalize the icosahedral series of gold cages is to gradually increase the distance between neighbouring five-membered rings. Au_{12} is composed of 12 fused five-membered rings. In Au_{32}, each of the 12 five-membered rings shares two atoms with each neighbouring pentagon, whereas in Au_{42}, each pentagon shares a single atom with each neighbouring pentagon. In Au_{72}, each atom of a pentagon is bound to two neighbouring pentagons through a triangle of three gold atoms (Fig. 1). Hence, the I-symmetric Au_{72} is the first member of the series to obey the isolated pentagon rule,[17] a structural feature familiar from the C_{60} fullerene,[1] and a major contributor to its unusual stability. As with the fullerenes, the fused pentagons introduce larger structural strain than the isolated ones. Beyond Au_{72}, the next member of the icosahedral series would be the previously reported Au_{92}.[7a] It is an open-shell system, however, and does not fulfil the criterion of spherical aromaticity.

In terms of total energies, the icosahedral Au_{72} is clearly favoured over the previously reported hollow gold cages (Table 1).§ Gibbs corrections to the total energies do not change the stability order (Table 1). The vibrational frequencies of Au_{72} range from 22 cm^{-1} to 163 cm^{-1}. The MP2 method appears to take the aurophilic attractions much more strongly into account than DFT, perhaps even overestimating the stabilising effect. It is notable that gold clusters with 72 atoms have been produced by pulsed laser vaporization but no attention has been paid to their molecular structures.[18] Photoelectron spectroscopic characterization of the clusters would be useful. As with Au_{32},[12] thermal effects are expected to play an important role, higher temperatures possibly favouring compact space-filling isomers. Hence, while the high stability of the I-symmetric Au_{72} is encouraging, further efforts are required to verify its true character in the potential energy surface. Nevertheless, vibrational frequency calculations verify the neutral icosahedral Au_{72} together with its Au_{72}^{-} and Au_{72}^{2-} anions as true local minima. The hollow structure of Au_{72} would furthermore offer the possibility of endohedral functionalization such as in W@Au_{12}.[16] Overall, Au_{72} appears to be a magic cluster: thermodynamically the most stable hollow gold cage reported to date.

Quantitative information on the degree of aromaticity in cage-like molecules can be obtained by calculating the values of Nucleus-independent Chemical Shifts (NICS) at the centre of the cage.[19] Hollow gold cages fulfilling the $2(N + 1)^2$ criterion of spherical aromaticity have previously been shown to possess very high NICS values,[7a,14] indicating high aromaticity. The NICS value calculated for the icosahedral Au_{72} at the BP86/def2-TZVP level of theory is −111 ppm, significantly higher than −76.7 ppm and −88.5 ppm obtained for Au_{32} and Au_{50} at the same level of theory (Table 1). This provides further evidence of spherical aromaticity in Au_{72}, as suggested by its high stability and the fulfilled $2(N + 1)^2$ criterion.

The calculated HOMO–LUMO gap of the Au_{72} cage is 0.72 eV, a large value for a metal cluster of this size. Population analysis shows the 12 atoms on C_5-axes to have a slight positive charge. If the 12 gold atoms are replaced by the more electropositive silver atoms, the gap grows from 0.72 to 1.07 eV. The tetrahedral Au_{20} has the largest calculated HOMO–LUMO gap amongst the studied cages, 1.91 eV, in agreement with the experimentally determined value of 1.77 eV.[9] The HOMO–LUMO gaps of the spherically aromatic Au_{32}, Au_{50} and Au_{72} cages decrease as a function of the cage size (Table 1), all yet being significantly larger than the gap of the Au_{42} cage lacking spherical aromaticity. The orbital structure of Au_{72} corresponds relatively well to the "genuinely magic"[20] single filling of s-type to h-type (l = 0 to 5) shells of the molecule, each Au atom contributing one 6s orbital and one valence electron. From the HOMO downwards, the group-I irreducible representations are: $(h + t_2 + t_1)$ (l = 5) + $(h + t_2 + g + g)$ (l = 4 and 3) + $(t_1 + h)$ (l = 1 and 2). The 6s–5d hybridization gets stronger when going down from the h HOMO. The a_1 orbital (l = 0) lies further down in energy. Hence, exactly

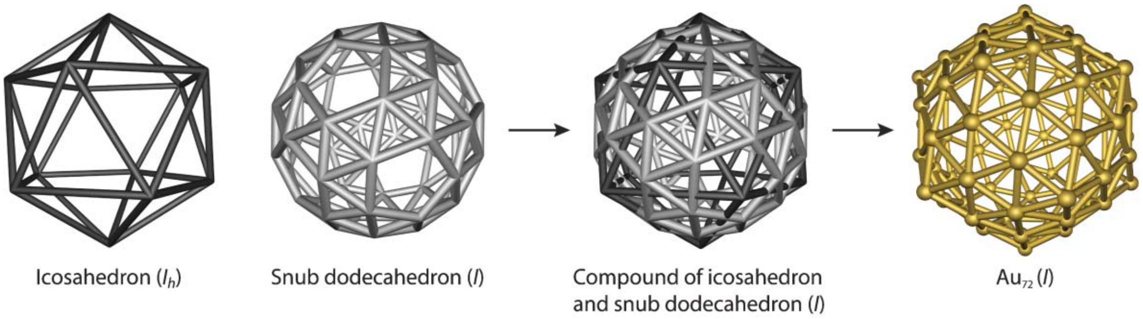

Fig. 2 Combining an icosahedron (12 vertices) with an I-symmetric snub dodecahedron (60 vertices) results in a chiral Au_{72} cage. The Au–Au bond lengths in Au_{72} vary from 2.75 to 2.84 Å.

the molecular orbitals that lead to a $2(N+1)^2$ system by filling the shells $l = 0$ to 5 can be identified, implying that 72 is not a "false magic number"[20] in the case of Au_{72}.

The combination of icosahedral symmetry and chirality in the Au_{72} cage, giving rise to the highest chiral point group of *I*, is notable and unusual. Although some virus particles form *I*-symmetric entities, little is known about small icosahedral molecules exhibiting chirality.[21] The theoretically predicted *I*-symmetric C_{140} fullerene[22] would be chiral, but it has not been experimentally characterized so far. The synthesis of the *I*-symmetric Au_{72} would thus produce the smallest known chiral molecule with icosahedral symmetry. Besides the distinctive structural peculiarity, the chiral Au_{72} could play a role as an enantioselective catalyst, small gold nanostructures showing catalytic activity.[6] Very recently, a chiral C_3-symmetric structure was proposed for Au_{34}^- cluster on the basis of experimental and theoretical evidence,[23] and enantiospecific adsorption on a chiral Au_{55} cluster has been demonstrated theoretically.[24]

In summary, we have described the structural principles of an icosahedral Au_{72} cage exhibiting both spherical aromaticity and chirality. Furthermore, Au_{72} is the smallest gold cage obeying the isolated pentagon rule essential for the stability of the fullerenes. Quantum chemical calculations show the hollow Au_{72} cage to possess high thermodynamic stability, a considerable HOMO–LUMO gap, and a large negative NICS value at the centre of the cage. Experimental synthesis of the *I*-symmetric Au_{72} would not only produce a novel golden nanostructure, but also an exceptional chiral molecule with icosahedral symmetry.

Notes and references

§ Computational details: The structures of the gold cages were fully optimised within their respective point group symmetries by using the BP86 density functional[25] and *ab initio* MP2 methods. Calculations were carried out with TURBOMOLE 5.9.1[26] and with a def2-TZVP basis set employing a 60-electron relativistic effective core potential for gold.[27] The resolution-of-the-identity technique was used to speed up both BP86[28] and MP2[29] calculations. BP86 vibrational frequency calculations were performed to confirm the vibrational stability of the cages and to obtain Gibbs free energies (T = 298 K, p = 0.1 MPa). Nucleus-independent Chemical Shift (NICS) values at the centre of each cage[19] were calculated with the Gaussian03[30] program at the BP86/def2-TZVP level of theory.

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