

Generation of isomers for icosahedral clusters $A_{12-x}B_x$ ($x = 0-12$) from a symmetry-based algorithm



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ABSTRACT

All isomers of (quasi-)icosahedral, binary $A_{12-x}B_x$ clusters were constructed based on a simple symmetry-based algorithm. This algorithm can also be applied to other starting geometries, but it is advantageous to restrict to high starting symmetries and high degeneracies of atom sites. Also, the (relative) degeneracies of the isomers are calculated. Chiral isomers are identified, showing that chirality in binary, (quasi-)icosahedral clusters may play an important role in A_8B_4 , A_7B_5 , A_6B_6 , A_5B_7 , and A_4B_8 . Chirality is of importance in nonlinear optics and asymmetric catalysis. The results provided may stimulate further research in these areas using binary metal clusters.

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1. Introduction

Metal clusters M_m are widely studied in both physics and chemistry. This is due to their intriguing, size- and structure-dependent properties [1–4], which give rise to interesting optical, magnetic and electronic effects. These are of interest in applications as contrast agents in imaging [5–8], catalysis [9,10], sensing [7], but also in answering questions in metallurgy, e.g. how many atoms must be present to observe metallic behavior? The continuing interest in metallic clusters is also partly owed to their fascinating structures, which often are derived from regular polyhedra, such as icosahedra, dodecahedra, cuboctahedra, etc.

The properties of a metal cluster M_m can be drastically altered when substituting one or several of the atoms by a foreign metal [11]. This gives rise to clusters $M_{m-x}M'_x$ (for convenience, we will use A for M and B for M' in the following). Continuous substitution, however, leads to a manifold of different isomers, which rapidly increase with the number of substitutions. For instance, the icosahedral A_{12} cluster has 12 equivalent atoms, which are located at the vertex sites of the icosahedron. Thus, substitution with one foreign atom B leads to one isomer $A_{11}B_1$. The second substitution gives three isomers of $A_{10}B_2$. In the next generation, $A_{10}B_3$, a manifold of isomers is to be expected. The identification of these is not straightforward, since different starting isomers may yield the same structure. It is intuitive to assume that the situation is even more complicated for higher generations of substitution.

Dass and co-workers recently presented the X-ray crystal structure of Ag-doped $Au_{25}(SR)_{18}$ clusters (SR: thiolate) [12]. The crystal structure determination yielded an average of 6.7 Ag atoms in all clusters, and the mass spectrometric analysis lead to a value of 6.2. From the mass spectra, it is obvious, that a mixture of clusters $Au_{25-x}Ag_x(SR)_{18}$ was obtained, with x ranging from 4 to 8. The basic structural features of the parent $Au_{25}(SR)_{18}$ cluster [13] are maintained: The cluster is composed of an icosahedral Au_{13} core (with a central atom), and the core is protected by six SR-(Au-SR)₂ motifs. The Ag atoms are located on the surface of the icosahedral core. This is in agreement with prior simulations, which predict this occupational behavior for doping thiolate-protected Au clusters with Ag [14,15]. Thus, the problem of isomerism can be reduced to the surface atoms of the $Au_{13-x}Ag_x$ core. Note that this substitution on the surface of the cluster core is unique to silver, e.g. palladium doping leads to substitution of the central atom [16]. Copper seems to occupy binding sites in the protecting SR-(Au-SR)_n motifs [17].

Along with the determination of the crystal structure of $Au_{25-x}Ag_x(SR)_{18}$, a density-functional theory (DFT) analysis of the Ag-doped clusters was provided [12]. Since the clusters co-crystallize in the same crystal, the data (and even less so mass spectrometry) do not provide information about the exact location of the Ag atoms and the distribution of the possible isomers for each substitution step. Instead, the crystal structure provides information about average Ag population of a specific site in the cluster. From this average population, a realistic and an artificial isomer of $Au_{19}Ag_6(SR)_{18}$ (which shows high abundance in the mass spectrum) was analyzed by means of DFT. Calculated absorption

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Table 1
Expected total degeneracies of each generation $G^{(x)}$ in (quasi-)icosahedral $A_{12-x}B_x$.

Cluster	$G^{(x)}$	$G(G^{(x)})$
A_{12}	0	1
$A_{11}B_1$	1	12
$A_{10}B_2$	2	132
A_9B_3	3	1320
A_8B_4	4	11,880
A_7B_5	5	95,040
A_6B_6	6	665,280

spectra of the two structures highlight the importance of the position of the Ag atoms in the doped Au cluster. However, a full theoretical analysis of all possible isomers of $Au_{19}Ag_6(SR)_{18}$ was not carried out. It should be mentioned that a vast number of isomers would have to be constructed and analyzed by DFT, which would lead to immense demand of computational resources.

The occupation of surface sites in the $Au_{13-x}Ag_x$ centered, quasi-icosahedral cluster has also been observed in early crystallographic work by Teo et al. on silver-doped phosphine-protected Au clusters ('clusters of clusters'). Bi- and triicosahedral clusters were analyzed crystallographically, and in all cases the central atom of the icosahedral building blocks was occupied by an Au atom [18–20]. A bicicosahedral binary kernel has also been observed in the crystal structure of $Au_{38-x}Ag_x(SR)_{24}$ [21].

The crystal structure of $Au_{25-x}Ag_x(SR)_{18}$ raises the question, how many geometric isomers are possible when the atoms of an icosahedral cluster A_{12} are subsequently substituted by foreign atoms B. To my knowledge, a thorough analysis of this problem has not been carried out to date. The position of foreign metals in clusters of high symmetry has implications on the point group symmetry of the obtained isomers. This is of particular importance in nonlinear optics, where second-order optical effects show a drastic dependence on the molecular symmetry [22].

Another prominent candidate for doping is the icosahedral Al_{13} cluster [23]. The cluster has characteristics of a 'super-halogen' and is easily reduced to the anionic species, which leads to 40-electron shell closing ($1S^2 1P^6 1D^{10} 2S^2 1F^{14} 2P^6$ in the superatomic picture). Doping of the cluster with foreign atoms has been discussed, but only cases of up to $Al_{11}M_2$ were considered [24–27]. The fact that

Table 2
Isomers and their characteristics for (quasi-)octahedral $A_{6-x}B_x$ ($x = 0, 1, 2, 3$) clusters.

Cluster	$G^{(x)}$	Number of Isomers	Point group	Rel. degeneracy	Full descriptor
A_6	$G^{(0)}$	1	O_h	1	$O_h(1/1^*6)$
A_5B_1	$G^{(1)}$	1	C_{4v}	1	$C_{4v}(6/1^*4, 1^*1)$
A_4B_2	$G^{(2)}$	2	D_{4h}	1	$D_{4h}(6/1^*4)$
A_3B_3	$G^{(3)}$	2	C_{2v}	4	$C_{2v}(24/2^*2)$
			C_{2v}	3	$C_{2v}(72/1^*2, 1^*1)$
			C_{3v}	2	$C_{3v}(48/1^*3)$

Table 3
Isomers of $G^{(0)}$ (A_{12}), $G^{(1)}$ ($A_{11}B_1$) and $G^{(2)}$ ($A_{10}B_2$), their point groups and degeneracies.

Cluster	$G^{(x)}$	Number of isomers	Point group	Rel. degeneracy	Full descriptor
A_{12}	$G^{(0)}$	1	I_h	1	$I_h(1/1^*12)$
$A_{11}B_1$	$G^{(1)}$	1	C_{5v}	1	$C_{5v}(12/2^*5, 1)$
$A_{10}B_2$	$G^{(2)}$	3	C_{2v}	5	$C_{2v}(60/1^*4, 3^*2)$
			C_{2v}	5	$C_{2v}(60/1^*4, 3^*2)$
			D_{5d}	1	$D_{5d}(12/1^*10)$

the Al_{13} superatom can be (isoelectronically) doped by foreign atoms, however, justifies the search for isomers of higher substitution.

A prominent related problem is that of the isomers of heterofullerenes. In these, carbon atoms in the C_n cage are substituted by foreign atoms, such as N, P, B, and (B, N) [28–32]. Especially in the case of isoelectronically (B, N)-substituted fullerenes, a broad variety of possible isomers has to be considered. In a classic example, $C_{60-2x}(BN)_x$ ($x = 1-7$) was investigated by Pattanayak et al., making use of two-dimensional representations of the fullerenes (Schlegel diagrams) [30].

The aim of this article is to provide an overview of all possible isomers for foreign atom doped (quasi-)icosahedral clusters. We restrict ourselves to binary systems $A_{m-x}B_x$. The strategy presented here is entirely based on symmetry arguments and does not provide information of the relative stability of the isomers. The algo-

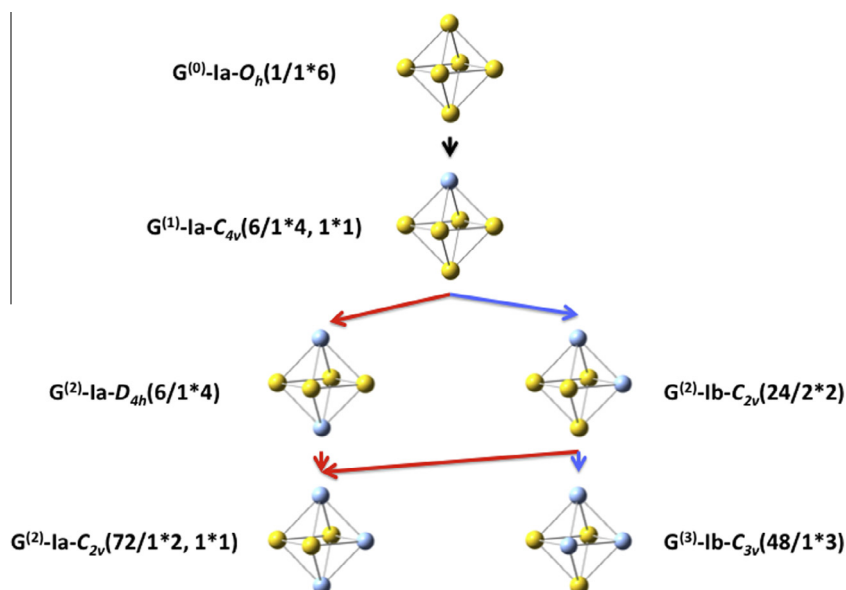


Fig. 1. Isomers and geometric characteristics of (quasi-)octahedral $A_{6-x}B_x$ clusters for $x = 0, 1, 2$, and 3. The relationships between the isomers in $G^{(x)}$ and $G^{(x-1)}$ are indicated by arrows.

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