Cooperative effect between electronic and geometric structures in binary clusters of superatoms
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The fabrication of cluster-assembled materials is dependent upon finding a suitable building block for a cluster that is chemically stable and that interacts weakly with other clusters of the same material. For designing the characteristics of clusters, binary systems are very important to create functionality of materials, and application of hetero-atom doping has been undertaken in the present study to two prototypes: metallic aluminum (Al) clusters and covalent silicon (Si) clusters. In particular, efforts to examine the superatom behavior involved in electronic and geometric shell closings have focused on substituting the central atom in Al$_{12}$X and MSi$_{16}$. Binary aluminum and silicon clusters of Al$_{12}$X and MSi$_{16}$ were generated by a double laser vaporization method, and the electronic and geometric stabilities for the resulting hetero-atom encapsulated clusters were examined experimentally. For aluminum-based binary superatoms of Al$_{12}$X, both experimental and theoretical results show that Al$_{12}$Si has high ionization energy and low electron affinity, and Al$_{12}$P has low ionization energy, both with the icosahedral structure having a central Si or P atom, revealing that Al$_{12}$Si and Al$_{12}$P exhibit rare-gas-like and alkali superatoms, respectively. Experiments confirmed the possibility that the change in the total number of valence electrons on substitution could produce ionic bound binary superatom complexes; the binary cluster salts (Al$_{12}$P)$^+$F$^-$ and (Al$_{12}$B)$^-$(Cs$^+$). For silicon-based binary superatoms of MSi$_{16}$, on the other hand, results obtained by mass spectrometry, anion photoelectron spectroscopy, and adsorption reactivity towards H$_2$O show that the neutral cluster doped with a group-4 atom features an electronic and a geometric closing at n=16. The MSi$_{16}$ cluster with a group-4 atom undergoes an electronic change in (i) the number of valence electrons when the metal atom is substituted by the neighboring metals with a group-3 or -5 atom, and in (ii) atomic radii with the substitution of the same group elements of Zr and Hf. The reactivity of a halogen atom with the MSi$_{16}$ clusters reveals that VSi$_{16}$F forms a superatom complex with ionic bonding.