Engineering Gold Superatoms with Electron Withdrawing Ligands

Heather Gaebler, Jenna Wilson and Julianna Castiglione

Department of Chemistry, Wilfrid Laurier University, ON, Email: gaeb1500@mylaurier.ca

Gold metallic clusters are a topic of considerable interest in the field of nanochemistry with significant resources devoted to understanding and perfecting their synthesis and characterization [1]. Nanoclusters exhibit novel properties resulting from strong quantum effects that differ from their bulk counterpart, and these properties can be fine-tuned by altering the shape, size, and composition of the cluster. Recently, it was discovered that certain stable clusters could imitate the chemical properties of noble gasses, and the term superatom was introduced. Superatoms have a stable configuration of electrons (2, 8, 18) for cage structures and (2, 8, 20) for compact structures that differs from the atomic series (2, 10, 18). This superatomic electron counting rule is an effective tool for interpreting geometrical structures and stability, as well as the chemical nature of cluster compounds [2]. This research project aims to engineer Au_4, and Au_{19}, and Au_{20} stable cage superatoms and compare their stabilities to the reference structures of Au_2 and the Au_{18} cage structure. For the gold atoms, each single 6s electron moves freely throughout the structure, therefore, to achieve the electron count of 2 and 18 the structures are modified through the addition of various electron withdrawing ligands, X, (where X = $-F^-$, $-Cl^-$, $-Br^-$, -I-, $-CN^-$, $-NO_2^-$, $-Ac^-$, $-OH^-$, $-OR^-$). The properties of the clusters are studied via density functional theory with a focus on analyzing spherical aromaticity through nucleus independent chemical shift (NICS) values, and chemical hardness through HOMO-LUMO gap energies. Results for the Au_4X_2, $Au_{19}X$, and $Au_{20}X_2$ clusters largely demonstrated that HOMO-LUMO gap energies increased when spherical aromaticity increased. When comparing the effects of adding the group 17 halogens, it was observed that spherical aromaticity and HOMO-LUMO gap energies increased when moving up the periodic table from iodide to fluoride. For the structures neutralized with the alkoxy ligand of varying length, it was determined that the chain length of the alkyl portion had no significant effect on the spherical aromaticity or HOMO-LUMO gap energies.

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[2] Walter, M., Akola, J., Lopez-Acevedo, O., Jadzinsky, P. D., Calero, G., Ackerson, C. J., Whetten, R. L., Grönbeck, H., Häkkinen, *H. Proc. Natl. Acad. Sci.* U S A. **105**, 9157–9162 (2008)