Au20. Effect of a Strong Tetrahedral Field in a Spherical Concentric Bonding Shell Model

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The tetrahedral Au20 cluster represents an outstanding landmark in cluster science. Its electronic structure can be described in terms of superatomic orbitals based on a 1s21p62s21d10 electronic configuration. Here we use the concentric bonding shell approach in order to rationalize Au20 in terms of a multilayered architecture accounting for its magic number of 20 valence electrons, which originates from the 2s antibonding combination between two structural layers. As the number of concentric structures increases from [Au4] ? [Au4@Au12] ? Au20, the superatomic shells are consequently expanded as, 1s1p ? 1s1p1d2s2p1f ? 1s1p2s1d2p3s1f3p. The role of spin-orbit coupling in affecting the electronic structure is also described. Our results suggest that Au20 can be conveniently viewed as the combination of concentric structures denoted by [{Au4@Au12}Au4] with considerable sharing of the electron density between the different concentric layers. Thus, the presence of the 2s antibonding combination originates from the interaction between two structural layers, ensuring the 20-ve count. Hence, both bonding and antibonding combinations of the s-type shells are populated, leaving both 1p and 1d shells as main superatomic bonding orbitals in the overall structure. Furthermore, the approach employed to rationalize the electronic structure of Au20 in terms of the interaction between layers is useful for the interpretation of larger thiolate-protected or bare gold clusters, among other species. (Figure Presented).