4-: Coinage Metal Tetrahedral Superatoms as Useful Building Blocks Related to Pyramidal Au20 Clusters (M = Cu, Ag, Au). Electronic and Bonding Properties from Relativistic DFT Calculations

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Characterization of the tetrahedral Au20 structure in the gas phase remains a major landmark in gold cluster chemistry, where further efforts to stabilize this bare 20-electron superatom in solution to extend and understand its chemistry have failed so far. Here, we account for the structural, electronic, and bonding properties of [M16Ni24(CO)40]4- (M = Cu, Ag, Au) observed in solution for gold and silver. Our results show a direct electronic relationship with Au20, owing that such species share a common tetrahedral [M16]4- central core with a 1S21P61D102S2 jellium configuration. In the case of Au20, the [Au16]4- core is capped by four Au+ ions, whereas in [M16Ni24(CO)40]4- it is capped by four Ni6(CO)10 units. In both cases, the capping entities are a full part of the superatom entity, where it appears that the free (uncapped) [M16]4- species must be capped for further stabilization. It follows that the Ni6(CO)10 units in [M16Ni24(CO)40]4- should not be considered as external ligands as their bonding with the [M16]4- core is mainly associated with a delocalization of the 20 jellium electrons onto the Ni atoms. Thus, the [M16Ni24(CO)40]4- species can be seen as the solution version of tetrahedral M20 clusters, encouraging experimental efforts to further develop the chemistry of such complexes as M(111) finite surface section structures, with M = Ag and Au and, particularly promising, with M = Cu. Furthermore, optical properties were simulated to assist future experimental characterization.