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Synthesis and Molecular Structure of Silver Cluster Having Phenylethynyl Groups as Bridging Units

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The families of Group-11 metal clusters are rapidly increasing in this decade because of their properties as functional materials for numerous applications, such as bioelectronics, sensing or catalysis. Compare to the gold clusters, examples of silver clusters are relatively limited. Here, we prepared a new silver cluster having a formula of $[Ag_{18}(CCPh)_{14}(PPh_3)_6(X)](SbF_6)_4$ by the reduction of $(AgCCPh)_n$ in the presence of $[Ag(PPh_3)]^+$, PhCCH, and NEt_3. The molecular structure of this silver cluster was determined by X-ray analysis as shown in Figure 1a. The cylindrical core part of the cluster consists of six (PhCC)Ag(CCPh) units as a wall and six Ag^+ cations inside of the wall as depicted schematically in Figure 1b. The top and bottom positions of this cylindrical core are occupied with PhCC ligands, and the wall of the cylinder is surrounded by six $Ag(PPh_3)$ units. The center of this cluster is occupied by a heteroatom which is not determined at this stage. This center atom X is surrounded twelve Ag^+ ions to form a cuboctahedral structure as shown in Figure 1c. There are a lot of examples in which twelve metals and a core atom form a regular dodecahedron structure. The present cluster is the second example of the silver cuboctahedral cluster. In the present case, six linear (PhCC)Ag(CCPh) units are assembled in a hexagonal style to lead the hexagonal packing of silver metals in the cuboctahedral structure.

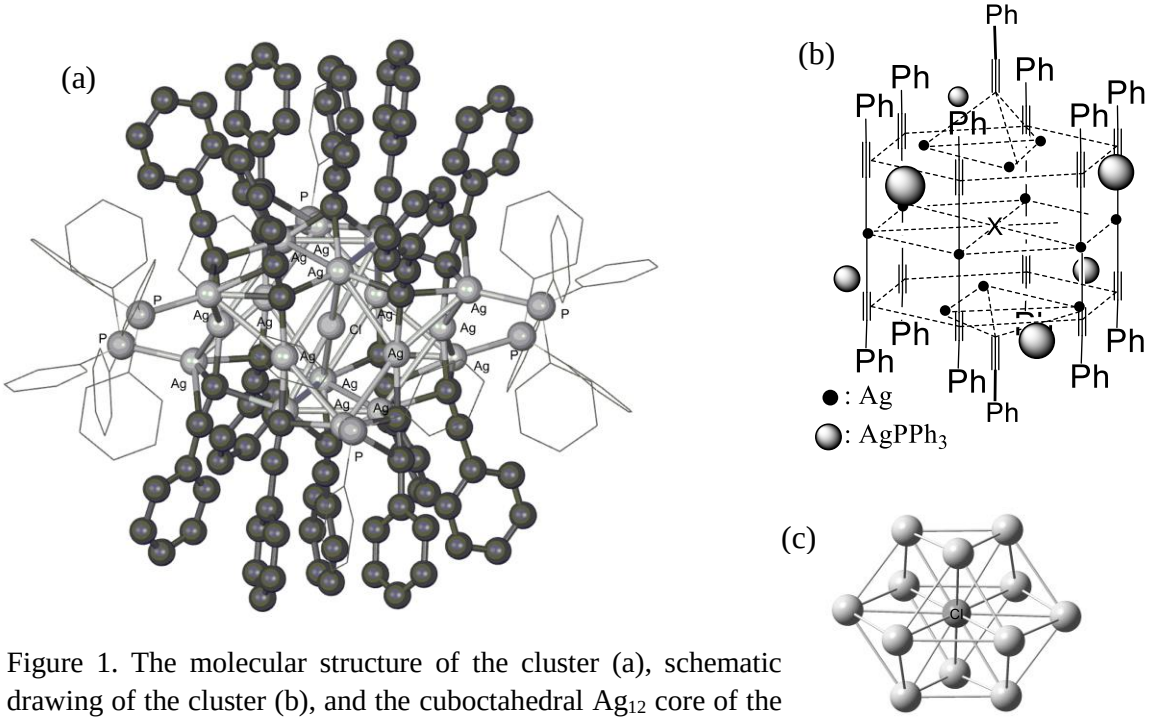

Figure 1. The molecular structure of the cluster (a), schematic drawing of the cluster (b), and the cuboctahedral Ag_{12} core of the cluster.