MULTIDECKER SANDWICH-LIKE COMPLEXES OF THE AROMATIC SQUARE AL_4^{2-} WITH GOLD.

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In the past few years, chemists have discovered several aromatic all-metal cluster systems [1-4]. The square planar Al_4^{2-} molecule constitutes one such example [1]. Different properties of Al_4^{2-} have been investigated: magnetic shielding [5], ring current [6], derived structures [7-8] and resonance energy [9-11]. The unusual high resonance energy of Al_4^{2-} has been attributed to the multiple-fold aromaticity, present in molecules that possess more than one independent delocalized bonding system, either σ- or π-type, each of them satisfying the 4n+2 electron counting rule. Furthermore, this cluster obeys the geometric criterion for aromaticity: it has a D_{4h} symmetric structure with all equal Al-Al bond lengths.

The Al_4^{2-} molecule is normally prepared as singly charged anion [1] due to large intramolecular Coulomb repulsion existing in the double charged molecule. At least one counterion is required to stabilize it in the form of MAl_4^-. Complexation with two counterions results in more stable species [9]. In this study, we stabilize the Al_4 square by complexation with two gold atoms ($AuAl_4Au$) keeping the whole system electrically neutral. Such complexation will induce aromaticity too.

Linear nanostructures are suggested to have a wide range of applications in nanotechnology. Metal nanowires in particular have been the focus of many researchers due to their potential applications in a field such as nanoelectronic circuits. In particular, a recent achievement is the fabrication of monoatomic gold wires, which can be produced in several ways like scanning tunneling microscopy (STM) [12]. The formation of free-standing chains of gold atoms between two bulk electrodes has been verified by high-resolution transmission electron microscopy (HRTEM) [13] and mechanically controlled break junction (MCBJ) experiments [14]. Our main interest is to investigate theoretically if ($AuAl_4Au$) units can be fused together in simple way to form large linear clusters or even polymers by means of Au-Au bonds.

$(AuAl_4Au)_n$ nanowires create a tremendous difficulty to theory due to the large number of atoms involved, their quasi-metallic character, and the presence of d electrons, which make the computations extremely demanding. We have performed DFT calculations using the well-tested SIESTA computer code [15]. Exchange and correlation effects were described using the generalized gradient approximation (GGA), within the Perdew-Burke-Ernzerhof (PBE) functional [16]. Such a choice of functional has been found adequate for the description of the geometric and electronic structure of gold nanowires [17]. The wire calculations were performed using standard double-ζ plus polarization basis set for infinite and finite chains of various lengths, ranging in size from 2 to 10 repeat units, using periodic boundary conditions. The distance between the wires in the supercell approximation was ca. 20 Å. In every case, the geometry was relaxed until the maximum forces were smaller than 0.04 eV/Å. The k-point sampling was (1×1×21) for the polymer calculation.

Our calculations demonstrate that Au metal can form highly linear multidecker complexes of formula $(AuAl_4Au)_n$ (Fig.1). These complexes may form large linear chains and eventually condense into one-dimensional polymers. There does not appear to be any fundamental limitation to the number of layers that can be fused, suggesting that one-dimensional multilayer compounds many nanometers in length could be synthesized. The structures predicted here await experimental verification.

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Figures:

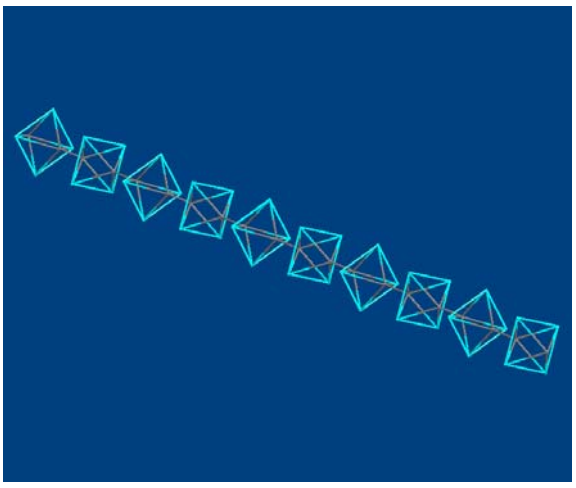

Fig. 1 Optimized structure of $(AuAl_4Au)_{10}$.

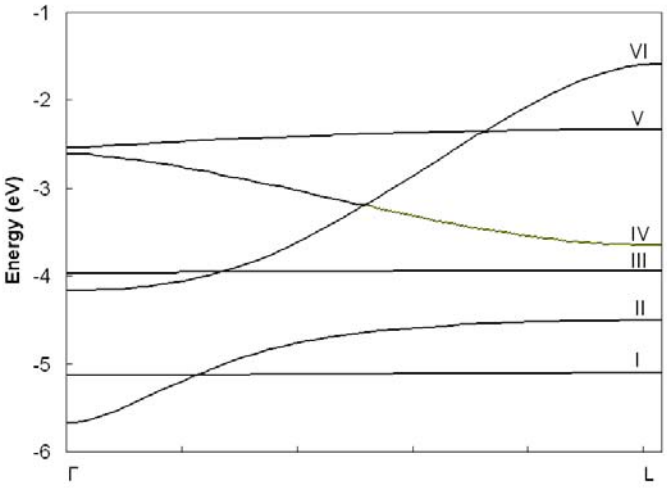

Fig. 2 The electronic band structure of the linear polymer $(AuAl_4Au)_\infty$. The Fermi level is at -3.95 eV.