MS43.O04

Assembly with Multinuclear Silver-Ethynediide/-Ethynide Supramolecular Synthons

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Over the past 15 years, our group has conducted a systematic investigation on the synthesis and structural characterization of a series of silver(I) double and multiple salts containing silver carbide Ag_2C_{2n} (n = 1, 2), in which the all-carbon dianion ethynediide C_2^{2-} is generally capsulated inside a polyhedral Ag_m (m = 6-10) cage, whereas C_4^{2-} exhibits variable coordination modes involving each terminal triple-bond and a Ag_m (m = 3-5) basket. Recently we reported the first successful synthesis of their unstable higher homologues Ag_2C_6 and Ag_2C_8, which were characterized through X-ray structure determination of their crystalline double salts $Ag_2C_6{\cdot}8AgCF_3CO_2{\cdot}6H_2O$, $4(Ag_2C_6){\cdot}16AgCF_3CO_2{\cdot}14.5DMSO$ and $2.5(Ag_2C_8){\cdot}10AgCF_3CO_2{\cdot}10DMSO$ (Figure 1).[1]

Our concomitant research program focused on silver(I) coordination and supramolecular network assembly based on multinuclear aggregates containing various kinds of carbon-rich ethynide ligands has established the robustness of *multinuclear metal-ligand silver-ethynide supramolecular synthons* symbolized as $C_2@Ag_n$ (n = 5-10), $Ag_4{\subset}C{\equiv}C{-}C{\equiv}C{\supset}Ag_4$, $Ag_n{\subset}C_6H_4$ (n = 7-9), $Ag_n{\subset}C{\equiv}C{-}R{-}C{\equiv}C{\supset}Ag_n$ (R = *o*-, *m*-, *p*-C_6H_4; n = 4, 5) and $R{-}C{\equiv}C{\supset}Ag_n$ (R = aryl, alkyl, heterocycle,…; n = 4, 5), which function as versatile structural building units for the construction of a variety of discrete molecules, high-nuclearity clusters,[2] as well as 1D-3D coordination and supramolecular architectures.[3]

In the absence of a definitive theoretical study, an empirical bonding model involving ionic, covalent and argentophilic interactions that consolidate the above-mentioned supramolecular synthons is proposed, which can account for the fact that analogous synthons have not been found for copper(I) and gold(I).

This work is supported by Hong Kong Research Grants Council GRF CUHK 402710.

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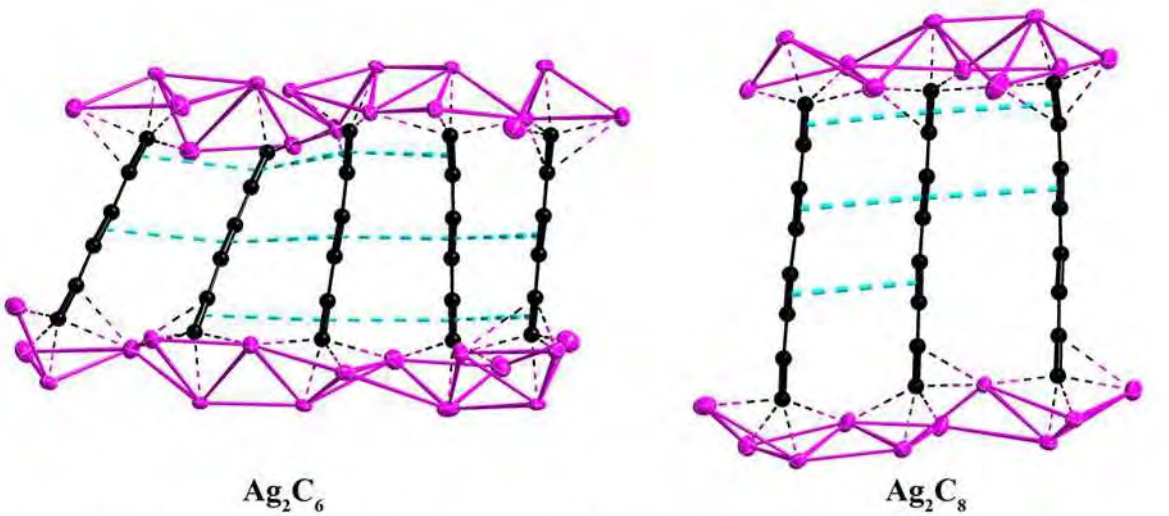

Figure 1. π–π Stacking modes of all-carbon ligands C_6^{2-} and C_8^{2-} in the multi-dimensional supramolecular architectures.

Keywords: argentophilicity, silver ethynide, supramolecular synthon, multinuclear