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New Polyoxometalate Species Stabilized in Coordination Networks Constructed with the Multinuclear Silver(I) Ethynediide Aggregate $C_2@Ag_n$ (n = 6 and 7)

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Three polyoxometalate-based silver(I) ethynediide complexes have been obtained by hydrothermal synthesis. New types of polyoxometalate motifs are generated and stabilized in a silver-rich environment in their respective three-dimensional coordination frameworks via assembly of the polyhedral metal−ligand $C_2@Ag_n$ (n = 6 and 7) supramolecular synthon.

Polyoxometalates constitute a rich and diverse class of inorganic clusters that exhibit fascinating structural, electrochemical, catalytic, magnetic, medicinal, and photophysical properties.[1] In view of the remarkable physical and chemical properties of metal oxide surfaces and the diversity in their geometric patterns, increasing recent interest has focused on the synthesis of new types of polyoxometalate systems and their use as secondary building units (SBUs) to construct higher-dimensional coordination frameworks.[2]

The study of alkyl and aryl ethynide complexes of the coinage metals (Cu, Ag, and Au) has experienced a renaissance, as evidenced by the increasing number of reports featuring M···M metallophilic interactions, as well as the potential application of such compounds in nonlinear optical materials, molecular wires, and molecular electronics.[3] In a parallel development, the synthesis and structural characterization of Ag_2C_2-containing complexes have yielded many fruitful results that are well documented.[4] A common structural feature of this class of compounds is the entrapment of the ethynediide species (C_2^{2-}) inside a silver(I) polyhedron, which can be symbolized as $C_2@Ag_n$ (n = 6−10).[4b] The construction of such cages relies on three synergistic factors: (i) Coulombic attraction, (ii) the versatile coordination modes of C_2^{2-} involving σ, π, and/or mixed (σ, π) Ag−C interactions, and (iii) argentophilicity, namely, the $d^{10}-d^{10}$ closed-shell attractive interaction that promotes the aggregation of Ag^I centers.

Given the increasingly large and impressive array of structural motifs exemplified individually by the polyoxometalates and silver ethynediide complexes, the conditions are ripe for the integration of both types of compounds for the design and development of new materials. Herein we present the synthesis and structural characterization of three polyoxometalate-based silver(I) ethynediide complexes, namely, $Ag_3(C_2)(VO_3)$ (**1**), $Ag_4(C_2)(V_2O_6)\cdot 0.5H_2O$ (**2**), and $Ag_6(C_2)(Mo_3O_{11})$ (**3**), wherein two principal SBUs, namely, polyoxometalate and condensed polyhedral $C_2@Ag_n$ clusters, coexist.

The double salt **1** was prepared by dissolving Ag_2C_2 in an aqueous solution of CF_3CO_2Ag and $AgBF_4$ followed by the addition of V_2O_5. The afforded precipitate was then subjected to hydrothermal conditions at 136 °C in a sealed tube to obtain **1** in ~15% yield. The structure of **1** exhibits a three-dimensional framework containing $(C_2)_4@Ag_{20}$ clusters, which features a honeycomb lattice stabilized by Ag···Ag and Ag−C interactions with entrapped $\{VO_3\}_\infty$ chains.

The $(C_2)_4@Ag_{20}$ cluster is composed of four vertex-sharing $C_2@Ag_6$ cages, each taking the shape of a quite distorted pentagonal pyramid (Figure 1a). The four enclosed C_2^{2-} dianions have C−C bond lengths of ~1.20 Å, which are in accordance with previous results reported for silver ethynediide

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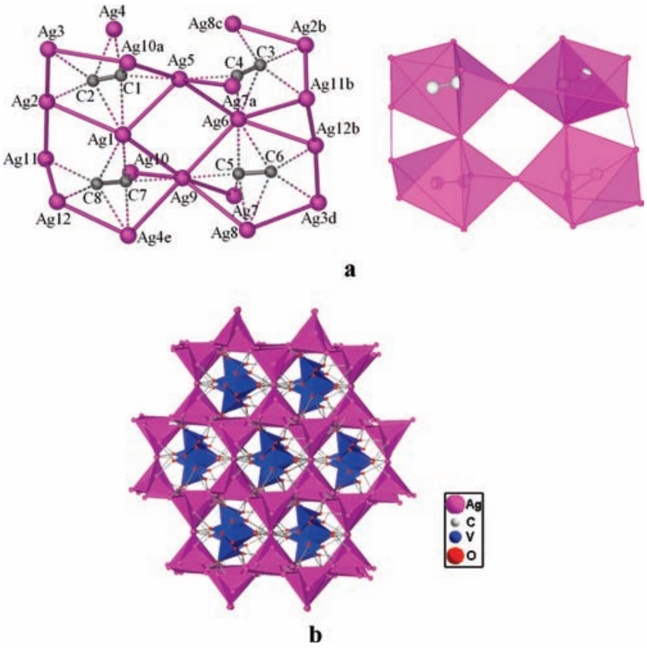

Figure 1. (a) Left: Silver(I) cluster $(C_2)_4@Ag_{20}$ in $Ag_3(C_2)_4(V_4O_{12})$ (**1**) constructed from vertex sharing of four $C_2@Ag_6$ cages viewed along the *b* direction. Symmetry codes: a, $x + {}^1/_2, y - {}^1/_2, z$; b, $x, -y + 1, z - {}^1/_2$; c, $x + 1, y, z$; d, $x - 1, -y + 1, z - {}^1/_2$; e, $x - 1, y, z$. Right: Polyhedral representation of the $(C_2)_4@Ag_{20}$ cluster in **1**. (b) Honeycomb-like three-dimensional framework generated from the fusion of $(C_2)_4@Ag_{20}$ clusters with $\{VO_3\}_\infty$ chains entrapped in its channels.

complexes.[4] The enclosed C_2^{2-} species coordinate to neighboring Ag^I atoms via multiple (σ, π) interactions in the range of 2.09(1)−2.53(2) Å. Such $(C_2)_4@Ag_{20}$ clusters share atoms of types Ag2, Ag3, Ag11, and Ag12 to form an argentophilic layer, which are further fused together via vertex sharing of Ag atoms of types Ag4, Ag8, Ag7, and Ag10 to generate a three-dimensional honeycomb framework containing a series of parallel channels (Figures 1b and S1 in the Supporting Information).

Another interesting aspect of **1** is the existence of a $\{VO_3\}_\infty$ zigzag chain built up from vertex sharing of $VO_2O^b{}_2$ (O^b = bridging O atom) tetrahedra (Figure S2 in the Supporting Information). The V atoms occupying four independent positions are each coordinated by two O and two O^b atoms in a distorted tetrahedron, with $V-O^b$ bond lengths of 1.78(1)−1.82(1) Å and V═O bond lengths of 1.60(1)−1.68(1) Å, and the O═V═O, O═V−O^b, and O^b−V−O^b angles are in the ranges of 107.7(7)−110.3(5), 107.2(6)−110.4(5), and 108.8(5)−111.6(7)°, respectively. The calculated bond valence sums[5] for V1, V2, V3, and V4 are 5.264, 5.117, 5.160, and 5.003, respectively, confirming that all V atoms are present in the pentavalent oxidation state. The same infinite chain has been observed in metavanadates M^IVO_3 (M^I = NH_4, K, Rb, Cs), dinegative metavanadates BaV_2O_6, and some compounds bearing mono- or divalent organic cations.[6] Each $\{VO_3\}_\infty$ chain is completely accommodated inside the above-mentioned hexagonal channel via Ag−O bonding in the range of 2.30(1)−2.592(9) Å (Figure 1b).

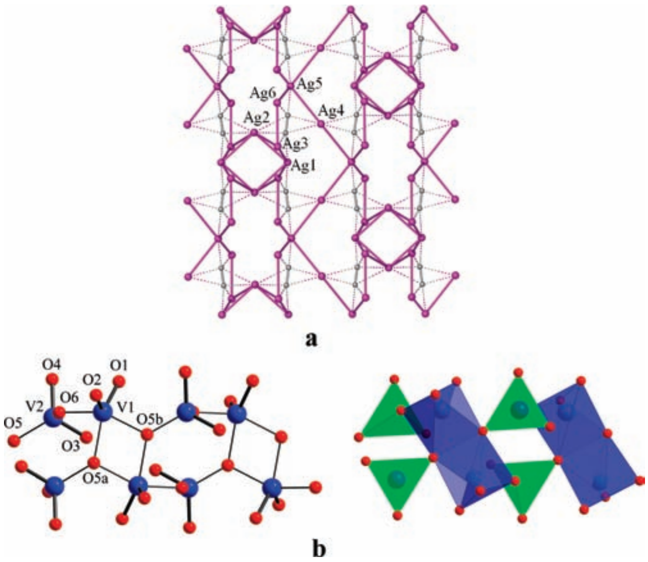

Figure 2. (a) Layer structure of **2** generated from silver(I) and ethynediide C_2^{2-} ions viewed along the *c* direction. (b) Left: Ball-and-stick model of the $\{V_2O_6\}_\infty$ ribbon in **2** generated from the fusion of $(VO_2O^b{}_3)$ square pyramids and $(VO_2O^b{}_2)$ tetrahedra. The V═O bonds are represented by bold lines. Right: Polyhedral representation of the $\{V_2O_6\}_\infty$ ribbon.

Compound **2** was synthesized in ∼10% yield following the procedure for **1**, with $AgClO_4$ replacing CF_3CO_2Ag. Its basic building unit is a $C_2@Ag_6$ cage in the shape of a distorted trigonal antiprism. Triangular faces Ag1Ag2Ag3 and Ag4Ag5Ag6 make a dihedral angle of 37.7°. The enclosed C_2^{2-} species [C−C bond length 1.21(1) Å] is stabilized by mixed (σ, π) Ag−C interactions in the range of 2.11(1)−2.63(1) Å. These silver cages are fused together via vertex sharing at atom types Ag1 and Ag5 to form an infinite column. Further vertex sharing at Ag2 and Ag4 results in a layer structure entirely composed of Ag^I and C_2^{2-} dianions (Figure 2a).

The oxovanadate component of **2** is a $\{V_2O_6\}_\infty$ zigzag ribbon built up from edge sharing of $VO_2O^b{}_3$ square pyramids connected by $VO_2O^b{}_2$ tetrahedra (Figures 2b). All of the V atoms are pentavalent, as confirmed by bond-valence-sum-calculated values of 5.010 and 5.151 for V1 and V2, respectively. The V═O bond distances in $VO_2O^b{}_3$ range from 1.613(7) to 1.678(7) Å, with one of the two O atoms occupying the axial position, while the longer V−O bond lengths vary between 1.891(7) and 2.048(7) Å. In the $VO_2O^b{}_2$ tetrahedron, the V═O double bond lengths are 1.638(8) and 1.650(8) Å, while the V−O^b single bond lengths are 1.768(7) and 1.816(7) Å. Pairs of adjacent VO_5 square pyramids are fused together via edge sharing and further connected by VO_4 tetrahedra via vertex sharing to give rise to an infinite ribbon. Oxovanadate structures are well documented, such as an infinite chain generated from corner sharing of VO_4 tetrahedra or a two-dimensional framework built up from the fusion of VO_5 square pyramids and VO_4 tetrahedra. However, to the best of our knowledge, the present $\{V_2O_6\}_\infty$ ribbon has no precedent in the literature.[7]

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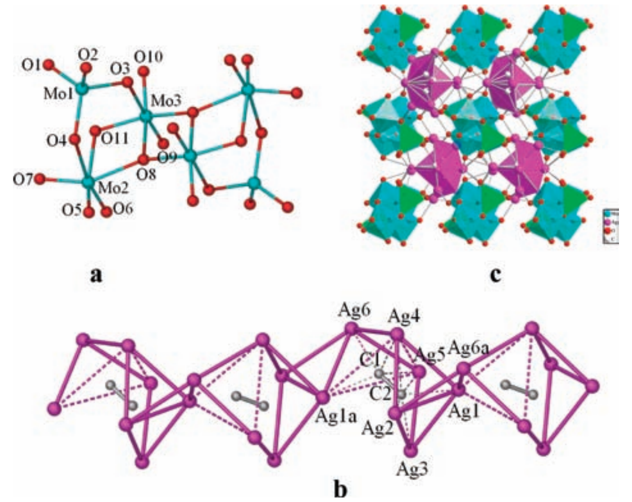

Figure 3. (a) Ball-and-stick model of the Mo_6O_{22} cluster constructed from two MoO_4 tetrahedra and four MoO_6 octahedra in **3**. (b) Infinite column of **3** generated via fusion of a $C_2@Ag_7$ single cage in the shape of a distorted monocapped trigonal antiprism. (c) Three-dimensional architecture of **3** generated from parallel silver(I) columns bridged by Mo_6O_{22} clusters.

Such $\{V_2O_6\}_\infty$ ribbons in **2** further connect with the silver(I) layers via Ag−O bonds in the range of 2.412(7)−2.591(8) Å to constitute a three-dimensional coordination network (Figure S3 in the Supporting Information).

When the synthetic procedure of **1** was repeated at 120 °C with $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ instead of V_2O_5, compound **3** was harvested. Although the synthetic preparation was reproducible, the yield remained low at ~11%, and the resulting crystals were always accompanied by powders of undetermined composition. Similar to the two previous cases, **3** is built of two SBUs: a Mo_6O_{22} anionic aggregate and a $C_2@Ag_7$ cage. The discrete molybdenum cluster Mo_6O_{22} is located at a crystallographic inversion center, with each half consisting of a $MoO_2O^b{}_2$ tetrahedron (Mo1) and two MoO_6 octahedra $[MoO_3O^b{}_2O^t$ (Mo2) and $MoO_2O^b{}_2O^t{}_2$ (Mo3); O^t = triply bridging O atom] fused together by edge/vertex sharing, as shown in the polyhedral representation and ball-and-stick plot in Figures 3a and S4 in the Supporting Information. Atom O8 is bonded to three Mo centers, whereas O4, O3, and O11 each bridges two Mo atoms. The remaining six O atoms, each bonded to only one Mo atom, are distributed among Mo1, Mo2, and Mo3 with bond distances in the range of 1.73(1)−1.77(1) Å. Generally, the Mo−O bonds are shorter when fewer metal atoms share one O atom. In the Mo_6O_{22} cluster, the mean Mo−O distance is 1.751 Å for the terminal O atoms, 2.03 Å for O atoms of the type O^b, and 2.06 Å for O atoms of the type O^t. The structural motif of the Mo_6O_{22} moiety built from edge/vertex sharing of two MoO_4 tetrahedra and four MoO_6 octahedra is unprecedented, although several complexes containing the Mo_6O_{22} aggregate but composed of six fused MoO_6 octahedra or constructed by vertex sharing of two MoO_6 octahedra with four MoO_4 tetrahedra have been reported previously.[8]

The $C_2@Ag_7$ single cage takes the shape of a distorted monocapped trigonal antiprism. The three edges Ag2···Ag4, Ag3···Ag5, and Ag1···Ag1a constitute the vertical sides of the trigonal antiprism, with Ag6 capping the triangular face Ag1aAg4Ag5. The mean deviation of the Ag^I atoms constituting the three rectangular faces of the trigonal prism lies in the range of 0.026−0.056 Å. A $C_2{}^{2-}$ species is accommodated in this cage with Ag−C bond lengths in the range of 2.19(2)−2.56(2) Å. Silver cages of this type are fused together via vertex sharing at Ag1, which together with linkages of types Ag2···Ag6a and Ag1···Ag6a form an infinite silver(I) column (Figure 3b). Finally, cross-bridging of parallel argentophilic columns by the Mo_6O_{22} clusters generates a three-dimensional coordination network (Figure 3c) with Ag−O bond lengths in the range of 2.21(1)−2.567(9) Å.

In summary, we have shown that it is practical to incorporate polyoxometalates into various argentophilic lattices constructed with the silver ethynediide aggregate. Furthermore, in the silver(I)-rich environment, new types of polyoxometalate motifs are generated in the assembly of extended three-dimensional coordination frameworks, such as the novel $\{V_2O_6\}_\infty$ zigzag ribbon in **2** and the Mo_6O_{22} cluster in **3** exhibiting a new architecture. Progress in this direction may pave the way for the synthesis of a growing family of polyoxometalate-based silver ethynediide complexes, as well as related compounds containing iso-[9] and heteropolyanions. The present study employing the polyhedral metal−ligand $C_2@Ag_n$ (n = 6 and 7) supramolecular synthon is complementary to our recent report of the acid-induced surface functionalization of high-nuclearity polyoxometalate anions with the $Ag_n\subset C{\equiv}C^tBu$ (n = 3 and 4) supramolecular synthon in an organic solution medium to yield neutral ellipsoidal clusters.[10]

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Supporting Information Available: Synthetic procedures, crystallographic data in CIF format for **1**−**3**, and additional structure plots (Figures S1−S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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