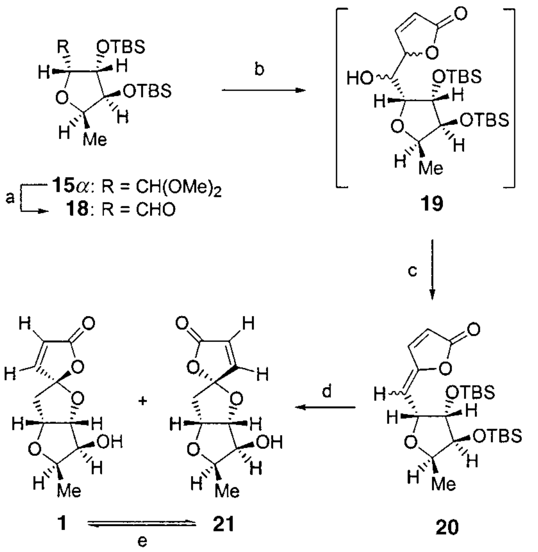

Scheme 5. a) TiCl$_4$, Et$_2$O, 0 °C, 88 %; b) 2-(trimethylsilyloxy)furan, BF$_3$·OEt$_2$, CH$_2$Cl$_2$, −78 °C; c) Burgess reagent, PhH, 55 °C, 80 % (two steps); d) 1N LiOH$_{aq}$, 23 °C; 16 % HF$_{aq}$, 23 °C, 93 % (1:1.4, **1/21**); e) 8N HCl$_{aq}$, THF, 23 °C, quant.

19, which was directly treated with the Burgess dehydrating agent (MeO$_2$CNSO$_2$NEt$_3$) to afford the unsaturated γ-lactone **20** (80 %, two steps) as a mixture of stereoisomers (2:1, *E*/*Z*). Formation of the spiroketal functionality and completion of the synthesis proceeded in a two-step, one-pot transformation from **20**, involving initial hydrolysis of the lactone (1N LiOH$_{aq}$), followed by acid-mediated (HF$_{aq}$) TBS-deprotection and spiroketalization to form a diastereomeric mixture of pyrenolide D (**1**) and its spiroketal epimer **21** in a 1:1.4 ratio (93 % total). Although the thermodynamic distribution of **1** and **21** exhibits essentially no selectivity, separation of the epimers by chromatography is trivial, allowing the quantitative iterative re-equilibration of **21** (8N HCl$_{aq}$, THF) to enhance the production of the natural product **1**. The spectral data (^{1}H and ^{13}C NMR, FTIR) of synthetic **1** derived from tri-*O*-acetyl-D-galactal coincide with those reported by Nukina and Hirota ($[\alpha]_D^{23} = +64.3$ ($c = 0.4$, CHCl$_3$), lit.: $[\alpha]_D^{23} = +79.5$ ($c = 0.9$, CHCl$_3$)).

In summary, the first synthesis of pyrenolide D (**1**) is described, involving a short sequence beginning with tri-*O*-acetyl-D-galactal. A key feature in the synthesis includes the efficient formation of highly functionalized tetrahydrofurfural intermediates directly from glycal substrates, by employing the reagent combination of iodosylbenzene and triflic anhydride in a mixture of methanol and dichloromethane. Not only did this process lead to the efficient synthesis and absolute stereochemical assignment of **1**, but it also highlights this oxidative ring contraction strategy as one that holds promise in both natural product and C-nucleoside synthesis.

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[12] It is likely that the triflic acid serves to activate the PhI(OMe)$_2$ reagent generated in situ.

[13] ^{1}H NMR analysis shows a relatively small H3–H4 proton coupling constant ($J_{3,4} = 2.8$ Hz). This is consistent with previous observations in other pyranosides incorporating vicinal *tert*-butyldimethylsilyl ethers in which *gauche* interactions between the bulky protective groups are minimized. See, for example: a) M. A. Tius, J. Busch-Peterson, *Tetrahedron Lett.* **1994**, *35*, 5181–5184; b) W. A. Roush, C. E. Bennett, *J. Am. Chem. Soc.* **1999**, *121*, 3541–3542.

[14] This rationale assumes, among other things, that the activation of gulal **12** proceeds irreversibly through a relatively late (i.e., C2-pyramidalized) transition state. For some discussions on the conformational flexibility of glycals, see: a) J. Thiem, P. Ossowski, *J. Carbohydr. Chem.* **1984**, *3*, 287–313; b) W. R. Roush, D. P. Sebesta, C. E. Bennett, *Tetrahedron* **1997**, *53*, 8825–8836.

[15] The employment of the *tert*-butyldimethylsilyl protecting groups was crucial in achieving the desired stereoselectivity. The use of dibenzyl-D-gulal with the identical oxidative ring contraction procedure led to indiscriminate facial approach of the I^{III} reagent, affording a 1:1 (α/β) mixture of the corresponding tetrahydrofurfural acetals in 82 % yield.

[16] Formation of the minor diastereomer **15β** might also arise from the β-approach of the oxidant onto **12** ($^5H_4$), leading to a higher energy twist-boatlike transition state. Following a conformational half-chair flip, ring contraction would lead to the minor diastereomer **15β**.

Crown-Ether-Directed Assembly of Discrete and One-Dimensional Silver Aggregates Containing Embedded Acetylenediide[**]

Quan-Ming Wang and Thomas C. W. Mak[*]

In memory of Daniel Y. Chang

Recent studies have shown that the coordination modes of the acetylide dianion (C$_2^{2-}$, IUPAC name acetylenediide) can be classified into three categories: 1) linear end-to-end

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bridging in the $\{[AgC_2]^-\}_\infty$ structure of ternary alkali metal silver acetylides $MAgC_2$ (M = Li, Na, K, Rb, Cs),[1] 2) planar μ_4-η^1,η^2 in the tetranuclear cation $[Cu_4(\mu\text{-dppm})_4(C_2)]^{2+}$ (dppm = bis(diphenylphosphanyl)methane),[2] 3) encapsulated inside a polyhedral Ag_n ($n = 6-9$) cage in a series of silver(I) double and triple salts.[3]

Thus far all reported compounds in category 3) have either layer-type or three-dimensional network structures, in which the component $C_2@Ag_n$ cages share common vertices or are linked by bridging anions. To obtain discrete molecules and infinite chains, our conceived strategy was to install protective cordons around the $C_2@Ag_n$ moiety with neutral, multidentate ligands that can function as blocking groups or terminal stoppers.

Bearing in mind that ancillary ligation of solvent may lower the dimensionality of a coordination polymer, we introduced crown ether into silver acetylide containing systems in an attempt to prevent catenation and interlinkage of the silver polyhedra. Notably, in the context of host–guest complementarity,[4, 5] the interaction of Ag^I with crown ethers is rather weak: a) there is poor affinity between hard oxygen donor and soft cation, and consequently only a few silver(I)–crown ether complexes have been reported;[6] b) the size of the Ag^I ion is too large to fit into the cavity of a crown ether, so that the host–guest system is necessarily forced to undergo distortion to accommodate the conflicting requirements of each partner.[7] Accordingly, crown ethers are expected not to affect the formation of $C_2@Ag_n$, but to act as weak capping ligands to provide ancillary ligation to the silver acetylide containing system. Herein we report the first isolation of discrete molecules and a zigzag coordination polymer containing embedded acetylide ions, for which [15]crown-5 (15C5) was employed as a structure-directing agent.

The crucial step in the synthesis of **1**–**3** took advantage of the fact that Ag_2C_2 readily dissolves in a concentrated aqueous solution of a silver(I) salt.[8] Although the mechanism of the dissolution is not clear, it is presumable that the rigid lattice of Ag_2C_2 breaks down with compensation by multiple argentophilic interactions[9] to form polyhedral species of the type $[C_2@Ag_n]^{(n-2)+}$ ($n \geq 6$). The crown ether then influences the assembly process of these species during crystallization. Different preparative procedures have led to the isolation of discrete molecules **1** and **2** and a zigzag polymeric chain in **3**.

$$[Ag_2C_2\cdot 5\,AgCF_3CO_2\cdot 2(15C5)\cdot H_2O]\cdot 3\,H_2O \qquad (\mathbf{1}\cdot 3\,H_2O)$$

$$[Ag_2C_2\cdot 6\,AgCF_3CO_2\cdot 2(15C5)\cdot H_2O]\cdot 0.5\,H_2O \qquad (\mathbf{2}\cdot 0.5\,H_2O)$$

$$[2\,Ag_2C_2\cdot 9\,AgCF_3CO_2\cdot 2(15C5)\cdot 2\,H_2O]_n \qquad (\mathbf{3})$$

The sandwiched molecular structure of **1** is shown in Figure 1. The silver cage enclosing an acetylide dianion is in the shape of a pentagonal bipyramid, with its two apices (Ag6 and Ag7) slightly shifted to one side of the idealized molecular axis. The equatorial silver atoms lie within 0.205 Å of their least-squares plane. Four of the five edges of the equatorial pentagon are each bridged by one trifluoroacetate ligand (tfa), the Ag3 ··· Ag4 edge being the exception. Ag3 is coordinated by one aqua ligand, and the tfa binding to Ag4 acts in a monodentate mode. Both Ag6 and Ag7 are each capped by one η^5-15C5 ligand, resulting in the first example of a discrete complex among silver acetylide containing systems.

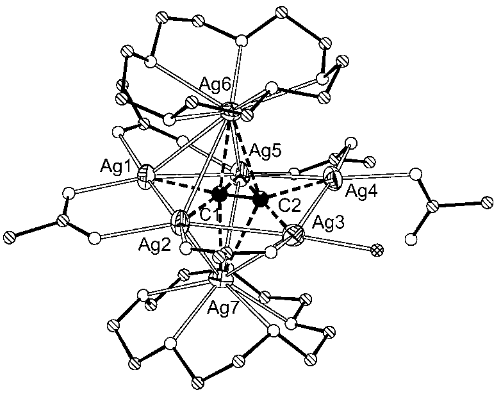

Figure 1. Crown-sandwiched molecular structure of compound **1** (the F and H atoms have been omitted for clarity). Range of metal–ligand distances [Å]: Ag-C 2.13–2.62; Ag-O 2.455–2.635 and 2.483–2.631 for the two crown ethers.

Interestingly, the sandwich unit in **2** is very similar to that in **1**. As shown in Figure 2, it also takes the shape of a pentagonal bipyramid but the two apices (Ag6 and Ag7) undergo a much larger lateral shift. As a result of such a distortion, the C_2^{2-} ion exhibits only π interactions with Ag5 and Ag7 (C1 does not bind to Ag6). This is different from the case in **1**, where the C_2^{2-} ion has π interactions with Ag5, Ag6, and Ag7. Another difference is that all edges of the equatorial pentagon in **2** are each bridged by one tfa ligand, and one corner atom is additionally coordinated by an aqua ligand. Two $[(\eta^5\text{-15C5})_2(C_2@Ag_7)(\mu\text{-}CF_3CO_2)_5(H_2O)]$ moieties are connected through a central $[Ag_2(tfa)_2]$ bridge to form a centrosymmetric hexadecanuclear supermolecule, as illustrated in Figure 3. Molecule **2** can be regarded as derived from **1** by linking two

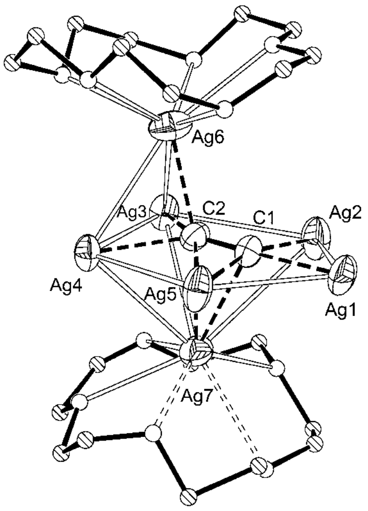

Figure 2. Sandwiched $C_2@Ag_7$ unit in compound **2**. Metal–ligand distances [Å]: Ag-C 2.118–2.555; Ag-O (crown ether) 2.443–2.635 and 2.524–2.743 Å. Two longer Ag–O bonds that exceed 2.7 Å are represented by broken open lines.

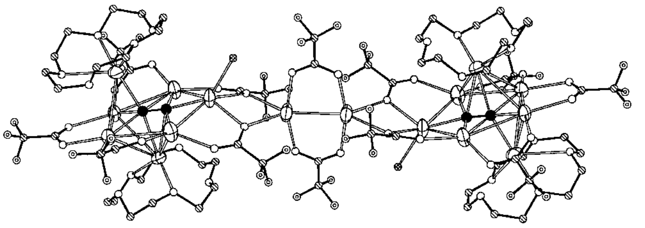

Figure 3. Centrosymmetric molecular structure of **2** (hydrogen atoms have been omitted for clarity): two sandwiched $C_2@Ag_7$ units and the central $[Ag_2(tfa)_2]$ bridge are linked by four μ_3-tfa ligands.

$C_2@Ag_7$ units through $[Ag_2(tfa)_2]$ bridging, and steric crowding leads to serious distortion of the polyhedral cage in **2**.

In contrast to the single silver cage in **1** and **2**, compound **3** contains a novel tridecanuclear double cage composed of two distorted square antiprisms that share a common triangular face Ag1-Ag4-Ag5 (Figure 4). For the upper antiprism, atom sets Ag1-Ag2-Ag3-Ag4 and Ag5-Ag6-Ag7-Ag8 constitute a pair of nearly parallel (dihedral angle 4.5°) tetragons, and for the lower one, the tetragons are made up of Ag4-Ag5-Ag12-Ag13 and Ag1-Ag9-Ag10-Ag11 (dihedral angle 3.5°). A unique feature is that both 15C5 ligands act in capping and bridging modes: for example, the upper 15C5 unit caps Ag7 and also bridges the Ag6⋯Ag7 edge through the binding of O025 to Ag6. Such a dual ligation mode is unprecedented in silver crown ether complexes. In the crystal structure of **3**, there are two nearly identical double cages in the asymmetric unit. As the molar ratio $15C5/C_2^{2-}$ is 1:1 in **3**, in contrast to 2:1 in **1** and **2**, there is sufficient room around each $(C_2)_2@Ag_{13}$ double cage to allow the approach of bridging tfa groups in the assembly of an infinite zigzag chain.

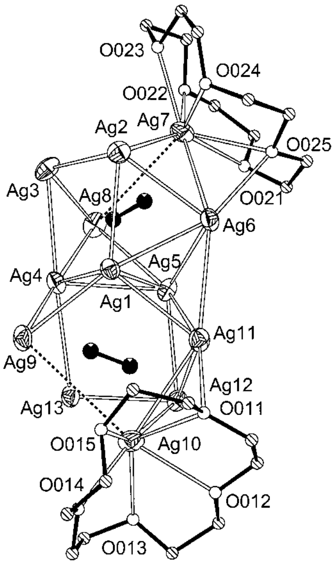

Figure 4. A sandwiched $(C_2)_2@Ag_{13}$ double-cage in **3**. Metal–ligand distances [Å]: Ag-C 2.12–2.70; Ag-O (crown ether) 2.416–2.694 and 2.437–2.696. The longer Ag⋯Ag distances that exceed 3.4 Å are represented by broken lines.

The C_2^{2-} species in **1**–**3** all retain their triple-bond character with the C–C bond length ranging from 1.13(1) to 1.26(1) Å, which are close to those in acetylene (1.205 Å)[10] and CaC_2 (1.191 Å).[11] The shortest Ag⋯Ag distances are 2.954(1) in **1**, 2.830(1) in **2**, and 2.847(1) Å in **3**, which are suggestive of significant argentophilic interactions.[12]

In conclusion, the assembly process of an acetylide-encapsulating silver cluster in an aqueous system that contains Ag_2C_2 can be affected by the presence of a neutral, multidentate ligand like a crown ether, leading to the generation of unusual structures of low dimensionality. The present study has thus established a new direction in silver acetylide chemistry, showing that the (η^5-15C5)Ag fragment is a potentially useful building block for the synthesis of silver clusters and supramolecular systems.

Experimental Section

Ag_2C_2 was prepared as described previously.[3] **Caution**: Thoroughly dried Ag_2C_2 detonates easily upon mechanical shock and heating, and only a small quantity should be used in any chemical reaction.

1: Ag_2C_2 was added to a concentrated aqueous solution of $AgCF_3CO_2$ (1 mL) in a plastic beaker with stirring until saturation. The excess amount of Ag_2C_2 was filtered off, and a few drops of 15C5 were added to the filtrate. The resulting suspension was transferred to a thick-walled glass tube. The tube was subsequently flame-sealed and kept in a furnace at 115 °C for 6 h, and then cooled down to room temperature at $6\,K\,h^{-1}$. Apart from a large quantity of black unidentified material, colorless platelike crystals of **1** were isolated in about 10% yield.

2: Ag_2C_2 was added to a concentrated aqueous solution of $AgCF_3CO_2$ and $AgBF_4$ (1 mL; molar ratio ~1:1) in a plastic beaker with stirring until saturation. The excess amount of Ag_2C_2 was filtered off, and a few drops of 15C5 ether were added to the filtrate. The resulting solution was allowed to stand without disturbance, and colorless blocklike crystals of **2** were obtained in over 50% yield after several hours.

3: Excess Ag_2C_2 and AgCN were added to a concentrated aqueous solution of $AgCF_3CO_2$ and $AgBF_4$ (1 mL; molar ratio ~1:1) in a plastic beaker with stirring until saturation. After filtration, a few drops of 15C5 were added to the filtrate. The resulting solution was placed in a desiccator charged with P_2O_5. The suspension that appeared overnight was transferred to a thick-walled glass tube. The tube was subsequently flame-sealed and kept in a furnace at 115 °C for 6 h, and then cooled down to room temperature at $6\,K\,h^{-1}$. Colorless prismatic crystals of **3** were isolated in about 30% yield.

Crystal data for **1**: $C_{32}H_{33}Ag_7F_{15}O_{24}$, $M_r = 1841.67$, monoclinic, space group $P2_1/c$ (no. 14), $a = 20.772(1)$, $b = 12.0453(7)$, $c = 22.041(1)$ Å, $\beta = 94.612(1)°$, $V = 5496.8(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.225\,Mg\,m^{-3}$, $F(000) = 3524$, $\mu(Mo_{K\alpha}) = 2.566\,mm^{-1}$. 36540 reflections measured, 13197 unique ($R_{int} = 0.0774$), final $R1 = 0.0465$, $wR2 = 0.1011$ for 4820 observed reflections ($I > 2\sigma(I)$).

Crystal data for **2**: $C_{34}H_{43}Ag_8F_{18}O_{23.5}$, $M_r = 2032.64$, monoclinic, space group $P2_1/n$ (no. 14), $a = 10.7506(5)$, $b = 20.2915(9)$, $c = 26.468(1)$ Å, $\beta = 94.225(1)°$, $V = 5758.2(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.345\,Mg\,m^{-3}$, $F(000) = 3892$, $\mu(Mo_{K\alpha}) = 2.792\,mm^{-1}$. 38492 reflections measured, 13873 unique ($R_{int} = 0.0357$), final $R1 = 0.0561$, $wR2 = 0.1610$ for 7034 observed reflections ($I > 2\sigma(I)$).

Crystal data for **3**: $C_{42}H_{44}Ag_{13}F_{27}O_{30}$, $M_r = 2944.08$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 16.533(1)$, $b = 25.235(2)$, $c = 35.007(2)$ Å, $V = 14605(2)$ Å^3, $Z = 8$, $\rho_{calcd} = 2.678\,Mg\,m^{-3}$, $F(000) = 11120$, $\mu(Mo_{K\alpha}) = 3.547\,mm^{-1}$. 98895 reflections measured, 35210 unique ($R_{int} = 0.0481$), final $R1 = 0.0466$, $wR2 = 0.1051$ for 19902 observed reflections ($I > 2\sigma(I)$).

Data collection was performed at 293 K on a Bruker SMART 1000 CCD diffractometer using frames of oscillation range 0.3°, with $1.5° < \theta < 28°$. The structures were solved by direct methods, and all non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 using the SHELXTL program.[13]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-152945 (**1**), CCDC-152946 (**2**), and CCDC-152947 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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