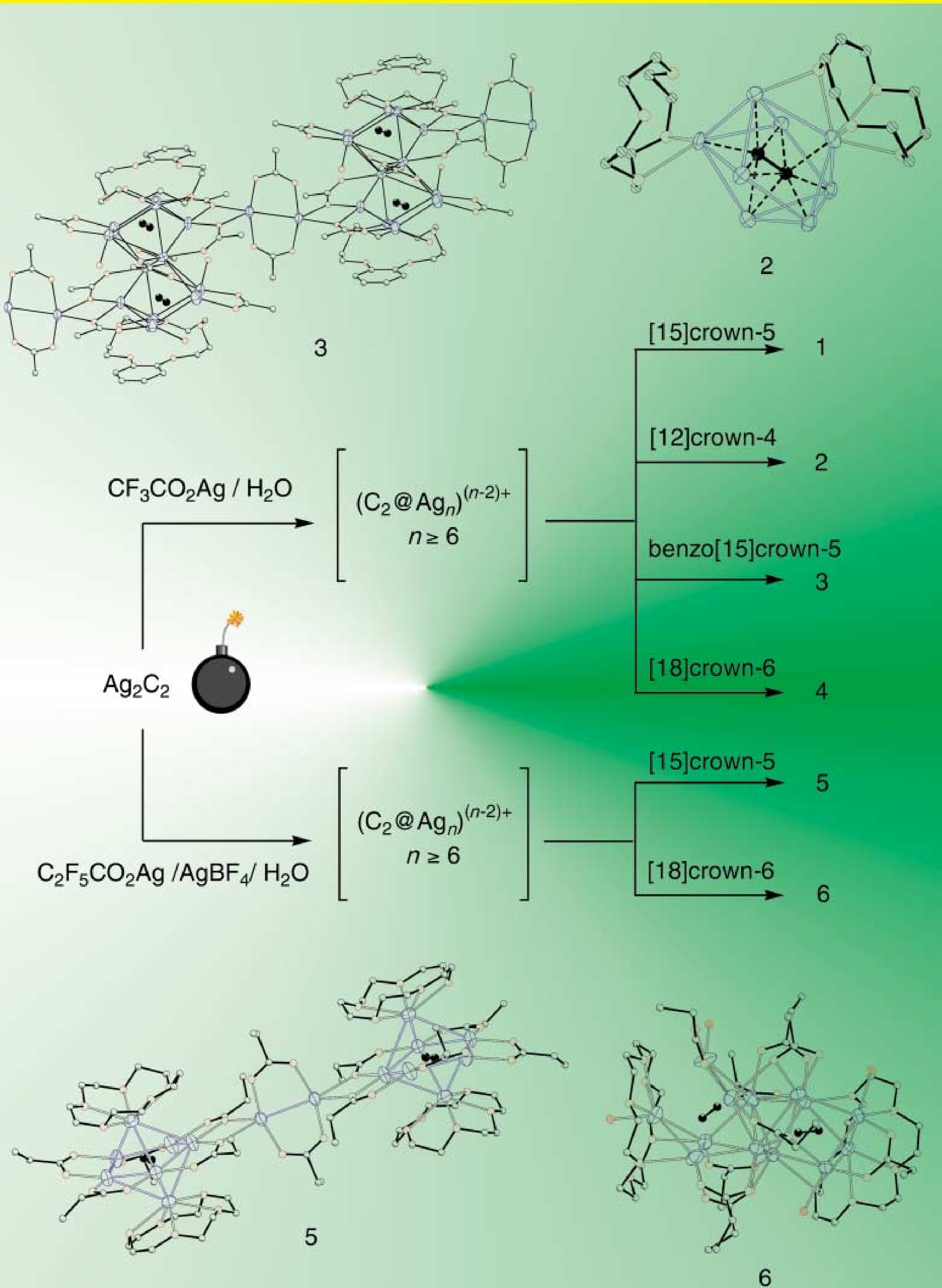


For more information see the following pages.

Crown Ethers as Ancillary Ligands in the Assembly of Silver(I) Aggregates Containing Embedded Acetylenediide

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

Dedicated to the memory of Dr. Daniel Y. Chang

Abstract: Five silver(I) double salts containing embedded acetylenediide, $[Ag([12]crown\text{-}4)_2][Ag_{10}(C_2)(CF_3CO_2)_9([12]crown\text{-}4)_2(H_2O)_3]\cdot H_2O$ (**2**), $[Ag_2C_2\cdot 5AgCF_3CO_2\cdot (benzo[15]crown\text{-}5)\cdot 2H_2O]\cdot 0.5H_2O$ (**3**), $[Ag_4([18]crown\text{-}6)_4(H_2O)_3][Ag_{18}(C_2)_3(CF_3CO_2)_{16}(H_2O)_{2.5}]\cdot 2.5H_2O$ (**4**), $[Ag_2C_2\cdot 6AgC_2F_5CO_2\cdot 2([15]crown\text{-}5)]_2$ (**5**), and $[(Ag_2C_2)_2\cdot (AgC_2F_5CO_2)_9\cdot ([18]crown\text{-}6)_2\cdot (H_2O)_{3.5}]\cdot H_2O$ (**6**), have been isolated by varying the types of crown ethers and anions employed. Single-crystal X-ray analysis has shown that complex **2** is composed of winding anionic chains with sandwiched $[Ag([12]crown\text{-}4)_2]^+$ ions accommodated in the concave cavities between them. In **3**, silver(I) double cages each sandwiched by a couple of benzo[15]crown-5 ligands are linked by $\{Ag_2(CF_3CO_2)_2\}$ bridges to form a one-dimensional structure. For **4**, an anionic silver column is generated through fusion of two kinds of silver polyhedra (triangulated dodecahedron and bicapped trigonal antiprism), and the charge balance is provided by aqua-ligated $[Ag([18]crown\text{-}6)]^+$ ions. Complex **5** is a centrosymmetric hexadecanuclear supermolecule composed of two $[(\eta^5\text{-}[15]crown\text{-}5)_2(C_2@Ag_7)(\mu\text{-}C_2F_5CO_2)_5]$ moieties connected through a $\{Ag_2(C_2F_5CO_2)_2\}$ bridge. Compound **6** is a discrete supermolecule containing an asymmetric $(C_2)_2@Ag_{13}$ cluster core capped by two [18]crown-6 ligands in μ_3-η^5 and μ_4-η^6 ligation modes.

Keywords: acetylide · carboxylato complexes · cluster compounds · crown compounds · silver

Introduction

Silver acetylide, Ag_2C_2, was first prepared as an insoluble white powder by Berthelot in 1866,[1] but its composition was not cleared up until Stadler's analytical identification in 1938.[2] The structure of Ag_2C_2 is still unknown due to its highly explosive nature and insolubility in common solvents. Most of the early investigations (late 1800s and early 1900s) dealt with the utilization of silver acetylide compounds as detonators. Over a half century ago, it was found that a series of double salts with the stoichiometric formula $nAg_2C_2\cdot mAgX$ could be prepared by passing acetylene into an aqueous solution of a soluble silver salt AgX, for example, $AgNO_3$, until saturation is reached, or by dissolving silver acetylide in a concentrated aqueous solution of AgX.[3]

The first structural report of a double salt of silver acetylide, $Ag_2C_2\cdot 6AgNO_3$,[4] in 1954 revealed a rhombohedral silver cage with an encapsulated acetylide dianion (C_2^{2-}, IUPAC name acetylenediide) . However, the dumbbell-like C_2^{2-} moiety was wrongly orientated in the unit cell; refinement of the structure in 1990 showed that the dianion is disordered about a crystallographic threefold axis.[5]

Since 1998, a wide range of double/multiple salts of silver containing silver acetylide as a component have been synthesized and characterized in our laboratory.[6] In addition, a series of ternary alkali metal silver acetylides $MAgC_2$ (M = Li, Na, K, Rb, Cs) has been reported.[7] Recently, we developed a strategy using crown ethers to function as blocking groups or terminal stoppers to install protective cordons around the polyhedral $C_2@Ag_n$ ($n \geq 6$) moiety so that the isolation of low-dimensional supramolecular entities can be achieved.[8] Judging from the host–guest complementarity of Ag^I with crown ethers,[9] their mutual interaction should be rather weak owing to poor affinity between the soft cation and hard oxygen donor. In fact, only a few silver(I)/crown ether complexes have been reported.[10] Accordingly, crown ethers are not expected to affect the initial assembly of $C_2@Ag_n$, but to act as weak capping ligands to provide ancillary ligation to the polyhedral silver cage.

Recently, by introducing [15]crown-5 into silver acetylide-containing systems to prevent catenation and interlinkage of the silver polyhedra, we obtained a discrete silver(I) aggregate $[Ag_2C_2\cdot 6AgCF_3CO_2\cdot 2([15]crown\text{-}5)\cdot H_2O]_2\cdot H_2O$ (**1**).[8] A natural follow-up is to study the influence of size of various crown ethers on the assembly process of the silver(I) aggregates each containing an embedded acetylenediide.

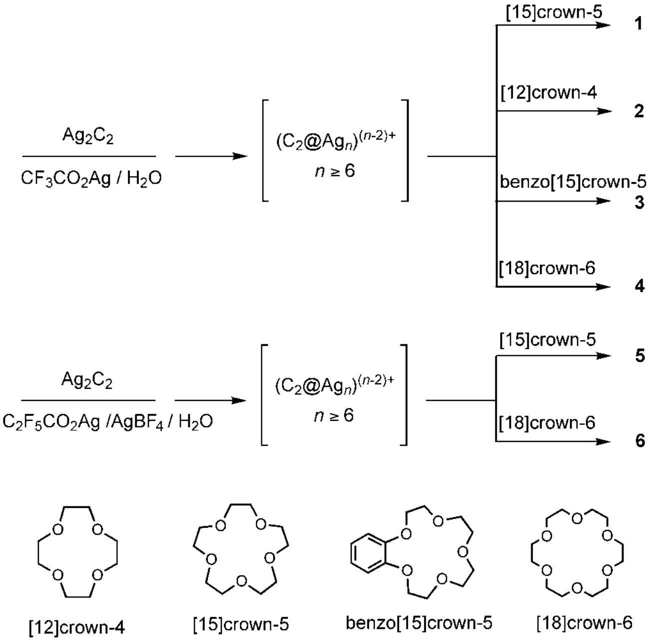
---

[a] Prof. T. C. W. Mak, Dr. Q.-M. Wang
Department of Chemistry
The Chinese University of Hong Kong
Shatin, New Territories, Hong Kong SAR (P. R. China)
Fax: (+852) 26035057
E-mail: tcwmak@cuhk.edu.hk

Furthermore, the effect of different co-existing anions is also a factor to be investigated. Herein we report the structural diversity of five new silver(I) aggregates: $[Ag([12]crown\text{-}4)_2][Ag_{10}(C_2)(CF_3CO_2)_9([12]crown\text{-}4)_2(H_2O)_3]\cdot H_2O$ (**2**), $[Ag_2C_2\cdot 5AgCF_3CO_2\cdot(benzo[15]crown\text{-}5)\cdot 2H_2O]\cdot 0.5H_2O$ (**3**), $[Ag_4([18]crown\text{-}6)_4(H_2O)_3][Ag_{18}(C_2)_3(CF_3CO_2)_{16}(H_2O)_{2.5}]\cdot 2.5H_2O$ (**4**), $[Ag_2C_2\cdot 6AgC_2F_5CO_2\cdot 2([15]crown\text{-}5)]_2$ (**5**), and $[(Ag_2C_2)_2\cdot(AgC_2F_5CO_2)_9\cdot([18]crown\text{-}6)_2\cdot(H_2O)_{3.5}]\cdot H_2O$ (**6**), which are generated by varying the types of crown ethers and perfluorocarboxylato anions used in the synthesis.

Results and Discussion

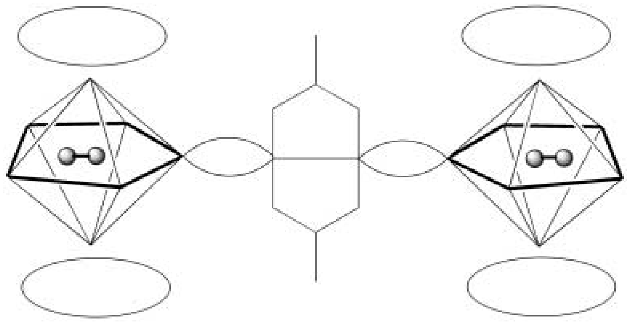
As described in our recent communication,[8] Ag_2C_2 readily dissolves in a concentrated aqueous solution of silver trifluoroacetate to form polyhedral species of the type $[C_2@Ag_n]^{(n-2)+}$ ($n \geq 6$). Introduction of a crown ether then affects the assembly process of these species during crystallization. The preparative procedure is shown in Scheme 1. From the same silver(I) starting materials, various crystalline double salts have been isolated under the structure-directing influence of different crown ethers: [12]crown-4, [15]crown-5, benzo[15]crown-5, and [18]crown-6. It is noteworthy that new aspects of structural diversity are observed in not only the crystal structures, but also the specific geometries of the silver cages.



Scheme 1.

Since the discovery of the first crown ethers by Pedersen,[11] their cation-binding behavior has been extensively studied.[12, 13] The cation-binding properties of crown ethers generally depend on three factors: 1) size compatibility between ring cavity and guest cation, 2) nature of ligating interactions, and 3) three-dimensional ligand topologies. Silver(I) is too large to fit into the cavities of [12]crown-4 and [15]crown-5, and thus sandwiched structures are expected to form. Although the size of silver(I) is about right for the cavity of [18]crown-6, mutual interaction is weak so that binding between them may be flexible.

The molecular structure of $[Ag_2C_2\cdot 6AgCF_3CO_2\cdot 2([15]crown\text{-}5)\cdot H_2O]_2\cdot H_2O$ (**1**), as depicted previously,[8] is a centrosymmetric hexadecanuclear supermolecule composed of two $[(\eta^5\text{-}[15]crown\text{-}5)_2(C_2@Ag_7)(\mu\text{-}CF_3CO_2)_5(H_2O)]$ moieties that are connected through a central $\{Ag_2(CF_3CO_2)_2\}$ bridge, of which a simplified illustration is shown in Scheme 2. With the ancillary ligation of [15]crown-5, complex **1** easily forms a crystalline solid in good yield.



Scheme 2.

When a smaller crown ether ([12]crown-4) is employed in place of [15]crown-5, not only are the sandwiched units retained, but additional host–guest interaction also occurs in the crystal structure of compound **2**, which is composed of a $[Ag([12]crown\text{-}4)_2]^+$ ion and a $[C_2@Ag_8([12]crown\text{-}4)_2(CF_3CO_2)_7]^-$ moiety. The structure of $[Ag([12]crown\text{-}4)_2]^+$, which occupies a site of symmetry m, is shown in Figure 1; one [12]crown-4 ligand is disordered over two equally populated sets of atomic positions. The coordination geometry at Ag8 is a distorted square antiprism formed by eight oxygen atoms of two [12]crown-4 ligands, whose square faces are twisted by about 31.5° from the eclipsed conformation; this is very similar to that (~30°) found in $[Ag([12]crown\text{-}4)_2][AsF_6]$.[10a] The Ag–O(crown) distances in the range 2.426–2.649 Å bracket the average value of 2.57 Å in $[Ag([12]crown\text{-}4)_2][AsF_6]$.

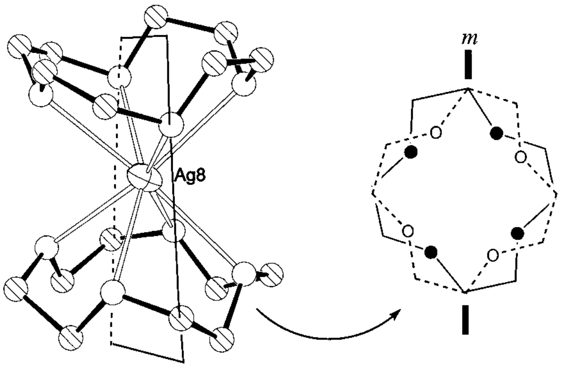


Figure 1. The sandwich structure of cation $[Ag([12]crown\text{-}4)_2]^+$, which occupies a site of symmetry m, in $[Ag([12]crown\text{-}4)_2][Ag_{10}(C_2)(CF_3CO_2)_9([12]crown\text{-}4)_2(H_2O)_3]\cdot H_2O$ (**2**). One [12]crown-4 ligand is disordered over two equally populated sets of atomic positions (shown in the right figure), and only one set is presented.

The fundamental building unit of **2** is shown in Figure 2. The silver cage enclosing an acetylenediide is in the shape of a triangulated dodecahedron, which possesses a mirror plane that cuts through the Ag1, Ag2, Ag3, Ag4, C1, and C2 atoms. Atom sets Ag1-Ag2-Ag3-Ag4 and Ag5-Ag6-Ag6a-Ag5a are thus each exactly coplanar, and the planes are perpendicular to each other (dihedral angle 90.0°). One acetylenediide moiety is encapsulated in the cage. The C–C bond length (1.18(1) Å) indicates that the C_2^{2-} species retains its triple bond character.[7, 14, 15] This is consistent with the case of previously reported silver acetylide-containing compounds.[16] The present C_2^{2-} ion is bound to all eight silver(I) atoms at Ag–C = 2.18(1) – 2.673(4) Å. The Ag···Ag distances lie in the range 2.854(1) – 3.320(1) Å, which are suggestive of significant argentophilic interactions.[17] The Ag2 and Ag4 atoms are each capped by one [12]crown-4 crown ether. There are seven trifluoroacetato ligands that bridge some of the Ag···Ag edges of the polyhedron to form an ionic moiety $[C_2@Ag_8([12]crown\text{-}4)_2(CF_3CO_2)_7]^-$. These moieties are connected through the $[Ag_2(CF_3CO_2)_2]$ (involving atom type Ag7) linkages to generate a winding, snake-like anionic chain. The $[Ag([12]crown\text{-}4)_2]^+$ ions occupy the concave cavities in the interchain region (Figure 3).

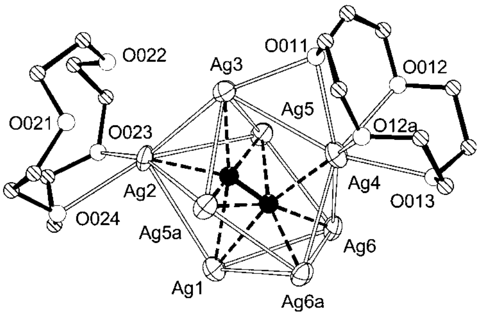


Figure 2. The triangulated dodecahedral silver cage with two capping [12]crown-4 ligands in **2**. The left [12]crown-4 ligand also exhibits disorder in a pattern similar to that in the last figure. The silver atoms are drawn as thermal ellipsoids at the 35% probability level. Selected bond lengths [Å]: C1–C2 1.18(1), C1–Ag1 2.38(1), C1–Ag4 2.25(1), C1–Ag5 2.673(4), C1–Ag6 2.201(7), C2–Ag1 2.57(1), C2–Ag2 2.18(1), C2–Ag3 2.21(1), C2–Ag5 2.407(1). Symmetry code: a) x, $1.5 - y$, z.

When benzo[15]crown-5 instead of [15]crown-5 was used in the reaction, neutral compound **3** crystallized as the product. The steric influence of the benzene ring along with the anticipated silver(I) – aromatic interaction[18] affect the assembly process, leading to the formation of a one-dimensional polymeric structure containing a double-cage fundamental unit. As shown in Figure 4 (left), this double cage can be viewed as two monocapped trigonal prisms sharing an Ag1–Ag1a edge. The geometry of the monocapped trigonal prism is shown in Figure 4 (right). Silver atom set Ag2-Ag3-Ag4-Ag1a-Ag5-Ag6 comprises a distorted trigonal prism with Ag1 capping the rectangular face Ag1a-Ag2-Ag4-Ag5. One C_2^{2-} species is encapsulated in this silver cage. Ag4 is coordinated by all five oxygen atoms of the benzo[15]-crown-5 ligand with bond lengths in the range 2.391 – 2.788 Å. Besides this, the double cage is further stabilized by the silver – aromatic interaction in the η^2 mode, with Ag3–C013 = 2.930 Å and Ag3–C014 = 3.084 Å. Although the Ag–C distances fall in the margin of significant Ag – C interaction,[19] statistical analysis has demonstrated that these longer contacts can be considered as weak interactions.[20] Each sandwiched double cage is linked to neighboring ones by $\{Ag_2(CF_3CO_2)_2\}$ bridges to form a one-dimensional structure, as illustrated in Figure 5.

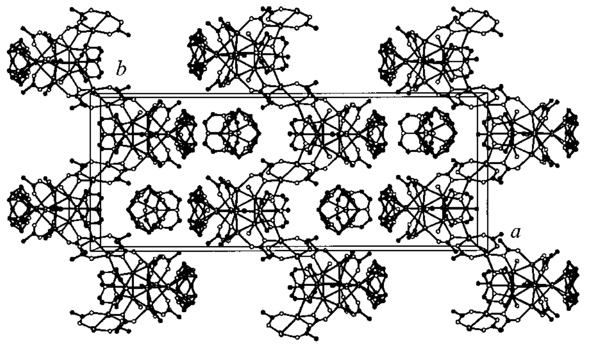


Figure 3. Crystal structure of **2**. Disordered crown ethers are each shown as a superposition of two sets of atomic positions. F atoms have been omitted for clarity.

When [18]crown-6 was employed in the reaction, complex **4** was isolated; this compound contains four independent $[Ag([18]crown\text{-}6)]^+$ ions and one $[Ag_{18}(C_2)_3(CF_3CO_2)_{16}$-

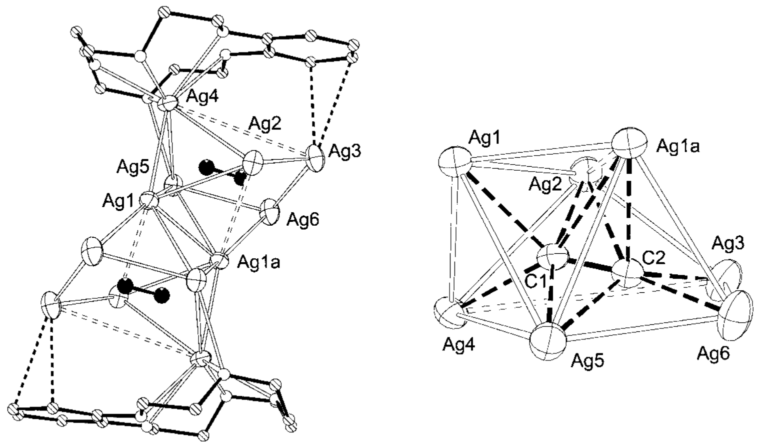


Figure 4. Left: Sandwiched double cage in $[Ag_2C_2 \cdot 5AgCF_3CO_2 \cdot (benzo[15]crown\text{-}5) \cdot 2H_2O] \cdot 0.5H_2O$ (**3**). The silver atoms are drawn as thermal ellipsoids at the 30% probability level, and the other atoms are represented by spheres. Right: Half of the double cage showing bonding interactions between the acetylenediide species and its surrounding silver(I) atoms. Ag···Ag distances (longer than 3.4 Å) are represented by broken open lines. Selected bond lengths [Å]: C1–C2 1.221(9), C1–Ag1 2.233(6), C1–Ag2 2.296(6), C1–Ag4 2.157(6), C1–Ag5 2.380(6), C1–Ag1a 2.693(6), C2–Ag1a 3.530(6), C2–Ag2 2.578(7), C2–Ag3 2.172(7), C2–Ag5 2.481(7), C2–Ag6 2.205(7). Symmetry code: a) $1 - x$, $-y$, $1 - z$.

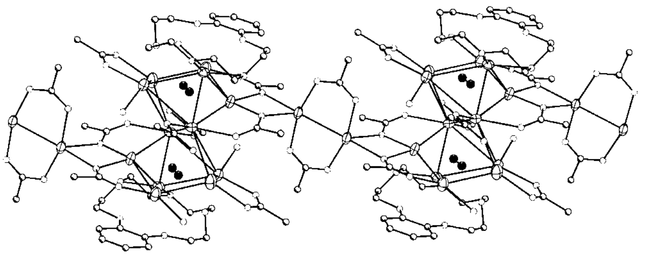


Figure 5. Chain structure in **3**, generated from sandwiched double cages connected by $\{Ag_2(CF_3CO_2)_2\}$ bridges. The silver atoms are drawn as thermal ellipsoids at the 35% probability level. Fluorine and hydrogen atoms have been omitted for clarity.

$(H_2O)_{2.5}]^{4-}$ moiety in the asymmetric unit. Unlike **1**–**3**, the anionic silver(I) aggregate has no [18]crown-6 component. The cationic part is composed of silver atoms each coordinated by a η^4-[18]crown-6 ligand (taking Ag–O distances below 2.8 Å as effective binding) and an additional aqua ligand in three of the four cases (Figure 6). The weak Ag^I–[18]crown-6 interaction is indicated by the longer Ag–O distances in the range 2.449–3.116 Å. The $[Ag([18]crown\text{-}6)]^+$ ions pack in stacks to induce the formation of an anionic column along the *a* direction (Figure 7).

A similar situation has been found in the mixed-valence silver(I,II) complex $[Ag^{II}(tmc)(BF_4)][Ag^I_6(C_2)(CF_3CO_2)_5(H_2O)]\cdot H_2O$ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane),[21] in which $[Ag^{II}(tmc)(BF_4)]_\infty^+$ constitutes a cationic column and no macrocyclic ligation occurs in the anionic zigzag chain constructed from edge-sharing of silver(I) triangulated dodecahedra each enclosing a C_2^{2-} species.

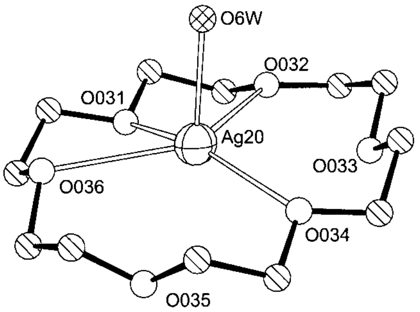


Figure 6. Structure of a $[Ag([18]crown\text{-}6)(H_2O)]^+$ ion in $[Ag_4([18]crown\text{-}6)_4(H_2O)_3][Ag_{18}(C_2)_3(CF_3CO_2)_{16}(H_2O)_{2.5}]\cdot 2.5\,H_2O$ (**4**). Aqua ligation appears in three of the four independent crown-complexed silver cations.

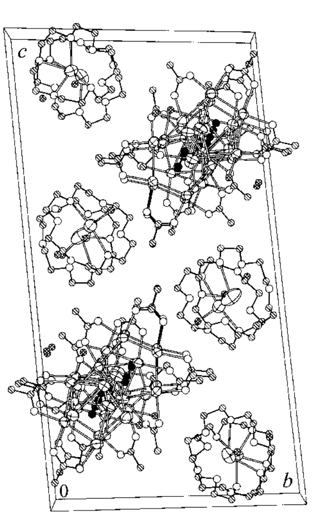


Figure 7. Molecular packing of **4**. The bonds between Ag atoms and the encapsulated C_2^{2-} are not shown, and F atoms have been omitted for clarity.

The silver column in **4** is generated through edge-sharing of two kinds of silver polyhedra. Two silver cages (**A** and **C**) are each in the shape of a triangulated dodecahedron and the third (cage **B**) is a bicapped trigonal antiprism, and thus the ratio of the former type to the latter is 2:1 (Figure 8). For cage **A**, atom sets Ag1-Ag2-Ag3-Ag4 and Ag5-Ag6-Ag7-Ag8 are each coplanar within 0.018 and 0.203 Å, respectively, making a dihedral angle of 94.6°. For cage **C**, atom sets Ag15-Ag16-Ag17-Ag18 and Ag14-Ag13-Ag5a-Ag6a are each coplanar within 0.026 and 0.058 Å, respectively, making a dihedral angle of 92.5°. For cage **B**, atom sets Ag7-Ag9-Ag10 and Ag11-Ag12-Ag13 make up a trigonal antiprism, and Ag8 and Ag14 each cap one triangular face. For cages **A** and **C**, each encapsulated C_2^{2-} species is bound to all eight silver(I) atoms at Ag–C = 2.17(1)–2.70(1) Å and 2.216(8)–2.632(9) Å, respectively. The C_2^{2-} unit in cage **B** is ligated to seven silver atoms with σ interactions except Ag8, and the shorter Ag–C lengths at 2.12(1)–2.430(9) Å can be attributed to the absence of π bonding. The Ag⋯Ag distances of the three silver polyhedra lie in the range 2.759(1)–3.319(1) Å. The silver polyhedra are connected to one another in the **ABCABC**… pattern, sharing edges of the type Ag5-Ag6, Ag7-Ag8 and Ag13-Ag14 to from the silver column.

Another factor we considered is the bulkiness of the hydrophobic group of the silver salt used to react with silver acetylide. Repeating the same procedure for the preparation of **1**, but by replacing trifluoroacetate with pentafluoropropionate, complex **5** was obtained. Its molecular structure is quite similar to that of **1**, being also a centrosymmetric hexadecanuclear supermolecule containing two sandwiched units. Each unit takes the shape of a pentagonal bipyramid, but there is no significant lateral shift of the two apices (Ag6 and Ag7), in contrast to the case in **1**. Each edge of the equatorial pentagon is bridged by one pentafluoropropionate ligand, and both Ag6 and Ag7 atoms are each capped by one η^5-[15]crown-5 ligand. Two $[(\eta^5\text{-}[15]crown\text{-}5)_2(C_2@Ag_7)(\mu\text{-}C_2F_5CO_2)_5]$ moieties are connected through a central $\{Ag_2(C_2F_5CO_2)_2\}$ bridge to form a centrosymmetric hexadecanuclear supermolecule, as illustrated in Figure 9. The Ag⋯Ag distance in the $\{Ag_2(C_2F_5CO_2)_2\}$ bridge is 2.875(1) Å, which is slightly longer than the corresponding value of 2.830(1) Å for $\{Ag_2(CF_3CO_2)_2\}$ in **1**.

In the case of **5**, the bulkiness of the $C_2F_5CO_2^-$ ion does not affect the resulting molecular structure, which bears a marked resemblance to that of **1**. However, when $C_2F_5CO_2^-$ was used in place of $CF_3CO_2^-$ in the preparation of **4**, to our surprise [18]crown-6 functions as a multidentate ligand to generate isolated silver(I) centers. The resulting compound **6** is a discrete supermolecule containing an asymmetric Ag_{13} cluster core, which is derived from the fusion of two types of silver polyhedra: a monocapped trigonal prism (**A**) and a bicapped trigonal antiprism (**B**), each enclosing an acetylenediide moiety (Figure 10). For cage **A**, the triangular faces Ag1-Ag2-Ag3 and Ag4-Ag5-Ag6 make a dihedral angle of 10.7°, and Ag7 caps the rectangular face Ag2-Ag3-Ag6-Ag5. For cage **B**, atom sets Ag7-Ag8-Ag12 and Ag10-Ag9-Ag11 form two triangular faces making a dihedral angle of 3.7°. Atoms

Ag6 and Ag13 cap the rectangular faces Ag7-Ag8-Ag9-Ag10 and Ag8-Ag9-Ag11-Ag12, respectively. Cages **A** and **B** share an edge Ag6–Ag7 to form an asymmetric silver double cage.

Another notable feature of **6** is that the capping [18]crown-6 ligands adopt two kinds of quite different ligation modes: μ_3-η^5 and μ_4-η^6 (Figure 11). The manifestation of these novel coordination modes may be attributed to the conformational flexibility of [18]crown-6 and the argentophilic, agglomerative tendency of silver(I).[17] A perspective view of this supermolecule is shown in Figure 12.

It is noteworthy that with the employment of the bulkier pentafluoropropionate, discrete supermolecules are formed with ancillary ligation of either [15]crown-5 or [18]crown-6. This is consistent with the finding in a previous example $Ag_2C_2 \cdot 9C_2F_5CO_2Ag \cdot 3MeCN \cdot H_2O$, which is also a discrete high-nuclearity cluster with acetonitrile as a terminal ligand.[22]

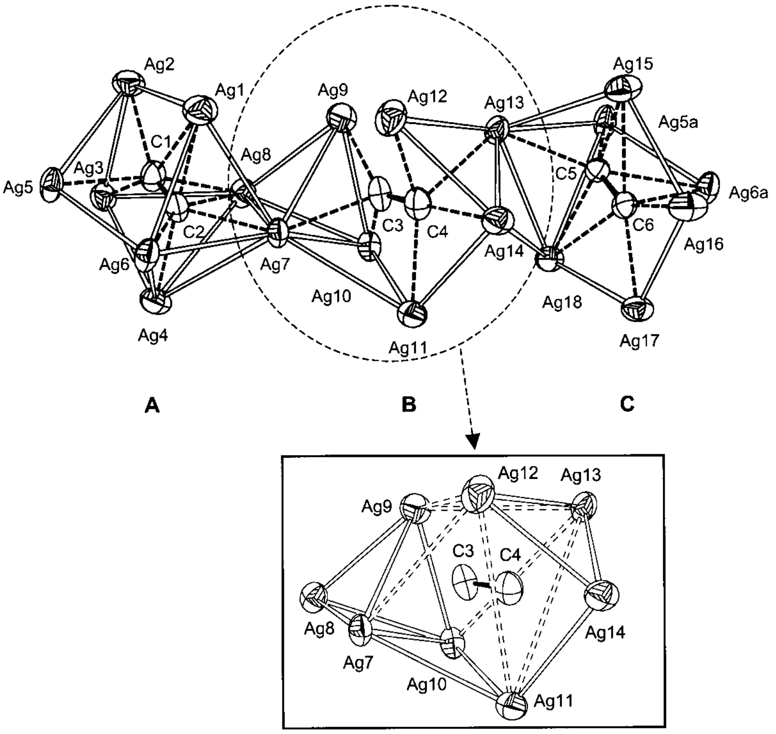


Figure 8. Trianglulated dodecahedra (**A** and **C**) and bicapped trigonal antiprism **B** (the capping atoms are Ag8 and Ag14) in **4**. Atoms are drawn as 30% thermal ellipsoids. Ag$\cdots$Ag distances (longer than 3.4 Å) are represented by broken open lines. Selected bond lengths [Å]: C1–C2 1.16(1), C1–Ag1 2.59(1), C1–Ag2 2.169(9), C1–Ag3 2.26(1), C1–Ag5 2.57(1), C1–Ag8 2.42(1), C2–Ag1 2.393(9), C2–Ag4 2.358(9), C2–Ag6 2.267(9), C2–Ag7 2.251(8), C2–Ag8 2.635(9); C3–C4 1.20(1), C3–Ag7 2.341(9), C3–Ag9 2.12(1), C3–Ag10 2.136(9), C4–Ag11 2.29(1), C4–Ag12 2.28(1), C4–Ag13 2.430(9), C4–Ag14 2.18(1); C5–C6 1.20(1), C5–Ag13 2.289(8), C5–Ag15 2.352(8), C5–Ag18 2.363(8), C5–Ag5a 2.216(8), C5–Ag6a 2.549(8), C6–Ag15 2.510(8), C6–Ag16 2.214(9), C6–Ag17 2.183(8), C6–Ag18 2.632(9), C6–Ag6a 2.517(8). Symmetry code: a) 1 + *x*, *y*, *z*.

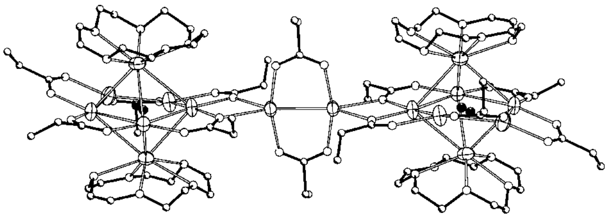


Figure 9. Centrosymmetric molecular structure of $[Ag_2C_2 \cdot 6AgC_2F_5CO_2 \cdot 2([15]crown\text{-}5)]_2$ (**5**): two sandwiched $C_2@Ag_7$ units and the central $\{Ag_2(CF_3CO_2)_2\}$ bridge are linked by four μ_3-$CF_3CO_2^-$ ligands. The silver atoms are drawn as thermal ellipsoids at the 35% probability level. F and H atoms have been omitted for clarity.

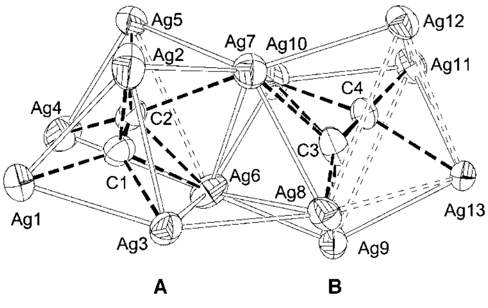


Figure 10. Cluster core of complex $[(Ag_2C_2)_2 \cdot (AgC_2F_5CO_2)_9 \cdot ([18]crown\text{-}6)_2 \cdot (H_2O)_{3.5}] \cdot H_2O$ **6**. Selected bond lengths [Å]: C1–C2 1.16(1), C1–Ag1 2.22(1), C1–Ag2 2.276(9), C1–Ag3 2.122(9), C1–Ag6 2.63(1), C2–Ag2 2.61(1), C2–Ag4 2.24(1), C2–Ag5 2.14(1), C2–Ag6 2.371(9), C2–Ag7 2.65(1); C3–C4 1.12(1), C3–Ag7 2.66(1), C3–Ag8 2.15(1), C3–Ag9 2.33(1), C3–Ag10 2.536(9), C4–Ag10 2.283(9), C4–Ag11 2.170(8), C4–Ag12 2.275(9), C4–Ag13 2.404(9).

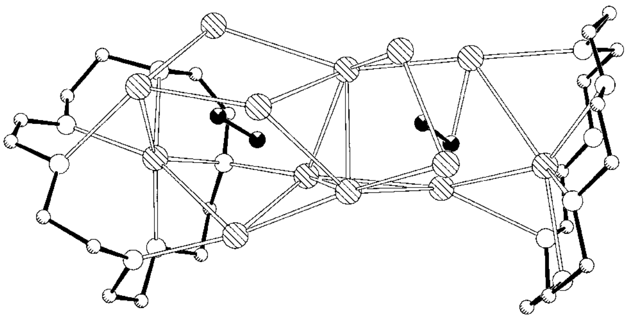


Figure 11. Two kinds of coordination modes, μ_4-η^6 (left) and μ_3-η^5 (right), displayed by [18]crown-6 in **6**. Large circles: silver; medium-sized circles: oxygen, small circles: carbon; black circles: C_2^{2-} species.

Conclusion

The loose coordination between crown ethers and silver(I) provides flexibility to the aggregation of the $C_2@Ag_n$ component with perfluorocarboxylates. In the present work, depending on the size of selected crown ethers, quite different crystal structures and silver polyhedral geometries are obtained. Besides the structural aspects, this work demonstrates that there is general applicability of the aforementioned synthetic strategy, and it is also evident that the extension from crown ethers to other macrocyclic ligands as protective cordons is worthy of further investigation.

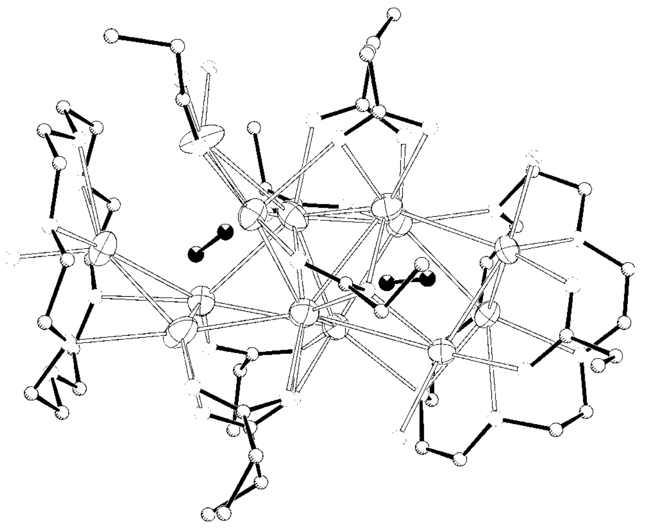


Figure 12. Perspective view of supermolecule **6**. F atoms have been omitted for clarity. The silver atoms are drawn as thermal ellipsoids at the 35% probability level. Open circles: oxygen; cross-hatched circles: aqua ligands; black circles: C_2^{2-} species; side-hatched small circles: other carbon atoms.

Experimental Section

General: Ag_2C_2 was prepared as described previously,[6] and other chemicals were used as purchased. **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. Excess amounts can be disposed in alkaline solution by slow decomposition.

Preparation of $[Ag([12]crown\text{-}4)_2][Ag_{10}(C_2)(CF_3CO_2)_9([12]crown\text{-}4)_2(H_2O)_3]\cdot H_2O$ (2): Ag_2C_2 was added to a solution of $AgCF_3CO_2$ (0.663 g, 3 mmol) in water (1 mL) in a plastic beaker with stirring until saturated. The excess amount of Ag_2C_2 was filtered off, and a few drops of [12]crown-4 ether (42 mg) 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 °CC for 6 h, and then cooled down to room temperature at 6° h^{-1}. Colorless platelike crystals of **2** were isolated in over 50% yield. Elemental analysis calcd (%) for $C_{52}H_{72}Ag_{11}F_{27}O_{38}$ (3004.67): C 20.79, H 2.42; found: C 20.65, H 2.34.

Preparation of $[Ag_2C_2\cdot 5AgCF_3CO_2\cdot(benzo[15]crown\text{-}5)\cdot(H_2O)_2]\cdot 0.5H_2O$ (3): Ag_2C_2 was added to a solution of $AgCF_3CO_2$ (0.663 g, 3 mmol) in water (1 mL) in a plastic beaker with stirring until saturated. The excess amount of Ag_2C_2 was filtered off, and benzo[15]crown-5 (45 mg) dissolved in hot ethanol (1 mL) was added to the filtrate. The resulting solution was allowed to stand without disturbance, and colorless rhombic plates of **3** were obtained in good yield (over 80%) after several hours. Elemental analysis calcd (%) for $C_{26}H_{25}Ag_7F_{15}O_{17.5}$ (1657.55): C 18.84, H 1.52; found: C 19.09, H 1.65.

Preparation of $[Ag_4([18]crown\text{-}6)_4(H_2O)_3][Ag_{18}(C_2)_3(CF_3CO_2)_{16}\cdot(H_2O)_{2.5}]\cdot 2.5H_2O$ (4): Ag_2C_2 was added to a solution of $AgCF_3CO_2$ (0.663 g, 3 mmol) in water (1 mL) in a plastic beaker with stirring until saturated. The excess amount of Ag_2C_2 was filtered off, [18]crown-6 (50 mg) was added and dissolved in the filtrate. The resulting solution was allowed to stand without disturbance, and colorless needle-like crystals of **4** were obtained in over 50% yield after several hours. Elemental analysis calcd (%) for $C_{82}H_{112}Ag_{22}F_{48}O_{64}$ (5454.90): C 18.94, H 2.07; found: C 18.93, H 1.76.

Preparation of $[Ag_2C_2\cdot 6AgC_2F_5CO_2\cdot 2([15]crown\text{-}5)]_2$ (5): Ag_2C_2 was added to a solution of $AgC_2F_5CO_2$ (0.544 g, 2 mmol) and $AgBF_4$ (0.389 g, 2 mmol) in water (1 mL) in a plastic beaker with stirring until saturated. The excess amount of Ag_2C_2 was filtered off, and [15]crown-5 (45 mg) was 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° h^{-1}. Colorless blocklike crystals of **5** were isolated in good yield (> 80%). Elemental analysis calcd (%) for $C_{80}H_{80}Ag_{16}F_{60}O_{44}$ (4611.36): C 20.84, H 1.75; found: C 20.54, H 1.76.

Preparation of $[(Ag_2C_2)_2\cdot(AgC_2F_5CO_2)_9\cdot([18]crown\text{-}6)_2\cdot(H_2O)_{3.5}]\cdot H_2O$ (6): Ag_2C_2 was added to a solution of $AgC_2F_5CO_2$ (0.544 g, 2 mmol) and $AgBF_4$ (0.389 g, 2 mmol) in water (1 mL) in a plastic beaker with stirring until saturated. The excess amount of Ag_2C_2 was filtered off, and [18]crown-6 (60 mg) was added to the filtrate. A white precipitate was deposited, which was allowed to stand still without filtration. The precipitate changed to colorless blocklike crystals of **6** after several days. Yield, about 40%. Elemental analysis calcd (%) for $C_{55}H_{57}Ag_{13}F_{45}O_{34.5}$ (3527.32): C 18.73, H 1.63; found: C 18.32, H 1.32.

X-ray crystallography: Data collection was performed at 293 K on a Bruker SMART 1000 CCD diffractometer ($\lambda = 0.71073$ Å) using frames of oscillation range 0.3°, with $1.5° < \theta < 28°$. An white empirical absorption correction was applied by using the SADABS program.[23] The structures were solved by direct methods, and non-hydrogen atoms were located from difference-Fourier maps. For **2**, **3**, **5**, and **6**, all non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 using the SHELXTL program.[24] Part of the atoms of [18]crown-6 in **4** were refined

Table 1. Crystal data for complexes **2**–**6**.

	2	3	4	5	6
formula	$C_{52}H_{72}Ag_{11}F_{27}O_{38}$	$C_{26}H_{25}Ag_7F_{15}O_{17.5}$	$C_{86}H_{112}Ag_{22}F_{48}O_{64}$	$C_{80}H_{80}Ag_{16}F_{60}O_{44}$	$C_{55}H_{57}Ag_{13}F_{45}O_{34.5}$
crystal system	orthorhombic	triclinic	triclinic	monoclinic	triclinic
space group	*Pnma* (No.62)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a [Å]	44.306(7)	13.359(2)	12.020(1)	24.374(1)	13.6133(8)
b [Å]	17.503(3)	14.059(2)	18.864(2)	10.8682(6)	14.0308(8)
c [Å]	10.977(2)	14.651(2)	35.036(4)	26.314(1)	25.705(2)
α [°]	90	115.240(2)	92.932(2)	90	82.508(1)
β [°]	90	101.703(3)	98.728(2)	107.207(1)	82.859(1)
γ [°]	90	108.588(2)	105.632(2)	90	83.756(1)
V [Å^3]	8513(2)	2167.1(5)	7526(2)	6658.6(6)	4808.7(5)
Z	4	2	2	2	2
T [K]	293(2)	293(2)	293(2)	293(2)	293(2)
μ [mm^{-1}]	2.614	3.228	2.932	2.452	2.744
ρ_{calcd} [gcm^{-3}]	2.344	2.540	2.407	2.300	2.436
reflections collected	56620	12068	51366	43881	32546
unique reflections	10701	9502	35792	15962	22713
data [$I > 2\sigma(I)$]	5207	6485	18814	7299	11573
parameters	707	596	1665	902	1334
R_1 (obs)	0.0510	0.0463	0.0633	0.0465	0.0640
wR_2 (all data)	0.1599	0.1379	0.2034	0.1535	0.2114

isotropically. Some of the aqua or water oxygen atoms in **2**, **3**, **4**, and **6** have half occupancies. The crystal data and details of refinement are given in Table 1.

CCDC-193509 (**2**), CCDC-193510 (**3**), CCDC-193511 (**4**), CCDC-193512 (**5**), and CCDC-193513 (**6**) contain the supplementary crystallographic data for the structures reported in this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/cont/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk).

Acknowledgement

Financial support from the Hong Kong Research Grants Council Earmarked Grant (CUHK 4268/00P) and a postdoctoral fellowship from The Chinese University of Hong Kong awarded to Q.-M. Wang are gratefully acknowledged.

---

[1] M. P. Berthelot, *Annalen* **1866**, *138*, 245.

[2] R. Z. Stadler, *Z. Gesamte Schiess- Sprengstoffwes.* **1938**, *33*, 269, 304, 344.

[3] R. Vestin, E. Ralf, *Acta Chem. Scand.* **1949**, *3*, 101 – 124.

[4] J. Osterlof, *Acta Crystallogr.* **1954**, *7*, 637.

[5] X.-L. Jin, G.-D. Zhou, N.-Z. Wu, Y.-Q. Tang, H.-C. Huang, *Acta Chimica Sinica* **1990**, *48*, 232 – 236.

[6] a) G.-C. Guo, Q.-G. Wang, G.-D. Zhou, T. C. W. Mak, *Chem. Commun.* **1998**, 339 – 340; b) G.-C. Guo, G.-D. Zhou, Q.-G. Wang, T. C. W. Mak, *Angew. Chem.* **1998**, *110*, 652 – 654; *Angew. Chem. Int. Ed.* **1998**, *37*, 630 – 632; c) G.-C. Guo, G.-D. Zhou, T. C. W. Mak, *J. Am. Chem. Soc.* **1999**, *121*, 3136 – 3141.

[7] W. Kockelmann, U. Ruschewitz, *Angew. Chem.* **1999**, *111*, 3697 – 3700; *Angew. Chem. Int. Ed.* **1999**, *38*, 3492 – 3495.

[8] Q.-M. Wang, T. C. W. Mak, *Angew. Chem.* **2001**, 113, 1164 – 1167; *Angew. Chem. Int. Ed.* **2001**, *40*, 1130 – 1133.

[9] a J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, **1995**; b) B. Dietrich, P. Viout, J.-M. Lehn, *Macrocyclic Chemistry*, VCH, Weinheim, **1993**.

[10] a) P. G. Jones, T. Gries, H. Grutzmacher, H. W. Roesky, J. Schimkowiak, G. M. Sheldrick, *Angew. Chem.* **1984**, *96*, 357 – 358; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 376; b) Z.-C. Liu, M.-C. Shao, *Acta Sci. Nat. Univ. Pekin.* **1987**, *6*, 17 – 23; c) P. D. Prince, J. W. Steed, *Supramol. Chem.* **1998**, *10*, 155 – 158.

[11] C. J. Pedersen, *J. Am. Chem. Soc.* **1967**, *89*, 2495 – 2496; C. J. Pedersen, *J. Am. Chem. Soc.* **1967**, *89*, 7017 – 7036.

[12] C. J. Pedersen, *Angew. Chem.* **1988**, *100*, 1053 – 1059; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1021 – 1027.

[13] *Cation Binding by Macrocycles* (Ed.: Y. Inoue, G. W. Gokel), New York, Marcel Dekkker, **1990**.

[14] G. Herzberg, J. W. T. Spinks, *Z. Physik* **1934**, *91*, 386.

[15] M. Atoji, *J. Chem. Phys.* **1961**, *35*, 1950 – 1960.

[16] a) Q.-M. Wang, T. C. W. Mak, *J. Am. Chem. Soc.* **2000**, *122*, 7608 – 7609; b) Q.-M. Wang, T. C. W. Mak, *J. Am. Chem. Soc.* **2001**, *123*, 1501 – 1502; c) Q.-M. Wang, T. C. W. Mak, *J. Cluster Sci.* **2001**, *12*, 391 – 398; d) Q.-M. Wang, G.-C. Guo, T. C. W. Mak, *J. Cluster Sci.* **2002**, *13*, 63 – 73; e) Q.-M. Wang, T. C. W. Mak, *Angew. Chem.* **2002**, *114*, 4309 – 4311; *Angew. Chem. Int. Ed.* **2002**, *41*, 4135 – 4137; f) Q.-M. Wang, T. C. W. Mak, *Chem. Commun.* **2002**, 2682 – 2683.

[17] a) M. A. Omary, T. R. Webb, Z. Assefa, G. E. Shankle, H. H. Patterson, *Inorg. Chem.* **1998**, *37*, 1380 – 1386; b) G.-C. Guo, T. C. W. Mak, *Angew. Chem.* **1998**, *110*, 3296 – 3299; Angew. *Chem. Int. Ed.* **1998**, *37*, 3183 – 3186; c) C.-M. Che, M.-C. Tse, M. C.-W. Chan, K.-K. Cheung, D. L. Phillips, K.-H. Leung, *J. Am. Chem. Soc.* **2000**, *122*, 2464 – 2468; d) M. A. Rawashdeh-Omary, M. A. Omary, H. H. Patterson, *J. Am. Chem. Soc.* **2000**, *122*, 10371 – 10380; e) Q.-M. Wang, H. K. Lee, T. C. W. Mak, *New J. Chem.* **2002**, *26*, 513 – 515.

[18] E. A. Griffith, E. L. Amma, *J. Am. Chem. Soc.* **1974**, *96*, 5407 – 5413, and reference therein.

[19] M. Munakata, L.-P. Wu, G.-L. Ning, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga, N. Maeno, *J. Am. Chem. Soc.* **1999**, *121*, 4968 – 4976.

[20] M. Mascal, J.-L. Kerdelhué, A. J. Blake, P. A. Cooke, *Angew. Chem.* **1999**, *111*, 2094 – 2096; Angew. *Chem. Int. Ed.* **1999**, *38*, 1968 – 1971.

[21] Q.-M. Wang, T. C. W. Mak, *Chem. Commun.* **2001**, 807 – 808.

[22] Q.-M. Wang, T. C. W. Mak, *J. Am. Chem. Soc.* **2001**, *123*, 7594 – 7600.

[23] G. M. Sheldrick, SADABS: Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen (Germany), **1996**.

[24] G. M. Sheldrick, SHELXTL 5.10 for Windows NT: Structure Determination Software Programs, Bruker Analytic X-ray Systems, Madison, Wisconsin (USA), **1997**.

Received: September 17, 2002 [F4432]