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Anion mediated structural motifs in silver(I) complexes with corannulene

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The synthesis of three new silver(I) complexes with corannulene is reported. In the crystal these complexes form extended networks of Ag^+ ions, corannulene nuclei, and counterions, similar to the networks reported for Ag^+ with other polynuclear aromatic hydrocarbons (PAHs). The preferred Ag^+–arene interaction is compared with the model developed by Kochi. The crystal motifs can be described by a classification scheme analogous to that developed by Etter for hydrogen-bonded networks in solids. The effect of counterion variation (ClO_4^-, $O_3SCF_3^-$, BF_4^-) is noted to be substantial. Thus, although one can categorize the various networks, it is hard to predict an expected packing pattern on the basis of preferred binding in the metal/organic complex alone.

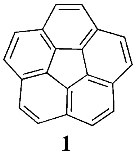
Introduction

The investigation of silver(I) complexes with arenes was initiated over 80 years ago by A. E. Hill.[1] Hill observed the high apparent molecular weights for silver perchlorate ($AgClO_4$) dissolved in benzene and rationalized this observation by suggesting the formation of polymeric silver–benzene arrays. Thirty years later the crystal structure of $C_6H_6{\cdot}AgClO_4$ was reported[2] and later fully refined.[3] The benzene–silver(I) complex consists of a W-shaped array of benzene–silver–benzene–silver–benzene chains and associated perchlorate counterions. Since that time, a wide variety of silver–arene crystalline arrays have been reported (Table 1). Kochi and co-workers examined a variety of silver–(mono)benzenoid ligand crystal structures reported in the Cambridge Structural Database[4] and identified three structural features common to all the complexes.[5] First, the perpendicular distance of the silver(I) atom from the mean plane of the coordinated arene (d) lies within the narrow range of 2.41 ± 0.05 Å (Fig. 1). Second, the angular parameter β, the angle between the central axis normal to the ring and the vector from the ring centroid to the silver atom, and the linear parameter Δ, the perpendicular distance from the silver atom to the central axis normal to the ring, show remarkable constancy ($\beta = 32° \pm 3°$ and $\Delta = 1.53 \pm 0.2$ Å; Fig. 1). Third, the preferred angle between benzenoid planes (α) falls into three sharply delineated ranges: 95°, 130°, and 155°; typically within ± 3° (Fig. 1). Additionally, Kochi noted that silver(I) forms exclusively η^1- or η^2-bonds to arenes.

Fig. 1 Key structural features of silver(I)–arene complexes ($d = 2.41 \pm 0.05$ Å, $\beta = 32° \pm 3°$, $\Delta = 1.53 \pm 0.2$ Å and $\alpha = 95$, 130, or 155° ± 3°).

A wide variety of planar and non-planar arenes have been used as ligands for silver complexation.[4–6] An examination of the Cambridge Structural Database reveals all of the four principal types of long-range structures arising from silver–arene complexation: discrete complexes formed from a small number of arene ligands (typically two to five), polymeric products that propagate in only one dimension (1-D), "cross-linked" polymers that propagate in two dimensions (2-D), and complex grids that propagate in three dimensions (3-D) see Table 1. Within these four classes of silver–arene complexes, several motifs are recurrent. The most common types of discrete structures are 3 : 1 inclusion complexes and 2 : 1 sandwich complexes, which may consist of parallel or perpendicular arene ligands (Fig. 2). 1-D polymers commonly form in one of six recurrent themes: double-layer, triple-layer, multi-layer, slipped double-layer, W-type, and inverting single-layer arrays (Fig. 3).[6] The double, triple, and multi-layer arrays are polymeric extensions of the parallel 2 : 1 sandwich complexes with counter-ions linking adjacent units. The W-type array, on the other hand, is a polymeric extension of the perpendicular 2 : 1 sandwich complex formed through direct arene–silver–arene–silver connectivity. The slipped double-layer array arises from a slight movement of one of the arene ligands in the double-layer array. This slippage causes a change in connectivity from sandwich units linked by counterions to direct arene–silver–arene–silver linkages. The inverting single layer array is a linear polymer of -(silver–counterion)- repeat units with coordinated arene ligands alternating above and below the plane of the polymer. 2-D and 3-D grids typically involve cross-linked versions of the 1-D polymeric structures described above. Munakata and co-workers, however, have elucidated two recurrent 2-D grids that are exceptions to this rule: the pillared brick array and the herringbone array (Fig. 4).

Despite the large number of structures reported, no complexes involving bowl-like fullerene fragments, specifically corannulene, have been reported. The following sections will analyze the results of co-crystallization of corannulene (**1**) and three different silver(I) salts in the context of counter ion *versus* arene structural effects.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Results

Corannulene·silver(I) perchlorate complex (2)

A co-crystal containing silver(I) perchlorate and **1** was grown from a 1 : 1 mixture of $AgClO_4$–$C_{20}H_{10}$ in toluene by slow vapor diffusion of hexanes. The crystals were grown in the absence of light in degassed vials under an atmosphere of argon gas to avoid photoreduction or hydrolysis of the complex. A single crystal

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Table 1 Silver–arene complexes and their long-range structures.

Discrete complexes	
Parallel 2 : 1 sandwich	
1.	$AgClO_4\cdot$indene[13]
2.	$AgClO_4\cdot$1,5-naphthaleno[2]paracyclophane[14]
3.	$Ag(OTf_3PtMe_3)\cdot$toluene[15]
4.	$Ag(Al(CH(CF_3)_2)_4)\cdot$toluene[16]
5.	$Ag(OTeF_5)\cdot$toluene[17]
6.	$AgClO_4\cdot$BINOL (benzene)[9]
7.	$AgClO_4\cdot$*o*-xylene[18]
8.	$Ag(L_1)\cdot$benzene[a] [19]
Perpendicular 2 : 1 sandwich	
9.	AgOTf$\cdot$2,3-bis(2,4,6-trimethylphenyl)bicyclo[2.2.2]oct-2-ene[5]
10.	AgOTf$\cdot$2,3-bis(pentamethylphenyl)bicyclo[2.2.2]oct-2-ene[5]
11.	$Ag(B_{11}CH_{10}F)\cdot$benzene[20]
12.	$AgClO_4\cdot$hexaphenylbenzene (acetone)[21]
13.	$AgClO_4\cdot$hexaphenylbenzene (THF)[22]
14.	$AgClO_4\cdot$cyclohexylbenzene[23]
3 : 1 Inclusion	
15.	$Ag(SbF_6)\cdot$bis([2.2.2]paracyclophane)butadiyne[24]
16.	$AgClO_4\cdot$5,12-methano[2.2.2]paracyclophane[25]
17.	$Ag(SbF_6)\cdot$*E*-2,3-bis([2.2.2]paracyclophane)but-2-ene[26]
18.	AgOTf$\cdot$[2.2.2]*m*,*p*,*p*-cyclophane[27]
19.	$Ag(SbF_6)\cdot$bis([2.2.2]paracyclophane)ethene[28]
20.	$Ag(SbF_6)\cdot$bis([2.2.2]paracyclophane)butadiene[28]
21.	$AgClO_4\cdot$tetraphenylethylene (xylene)[29]
22.	AgOTf$\cdot[2_6]$(1,2,4,5)cyclophane[30]
23.	AgOTf$\cdot$[2.2.2]paracyclophane[30]
24.	$Ag(SbF_6)\cdot$[2.2.2]paracyclophane[31]
25.	$AgClO_4\cdot$[2.2.2]paracyclophane[32]
26.	$Ag(L_2)\cdot$toluene[b] [33]
27.	$AgClO_4\cdot$diphenylacetylene (benzene)[34]
28.	$AgBF_4\cdot$benzene-d_6[35]
Miscellaneous	
29.	AgOTf$\cdot$[2.2.1]paracyclophane (H_2O)[36]
30.	AgOTf$\cdot$[2.2.1]paracyclophane[36]
31.	$Ag(B_{11}CCl_{11})\cdot$*p*-xylene[37]
32.	$Ag(Co(B_9CH_9)_2)\cdot$*p*-xylene[19]
33.	$AgClO_4\cdot$benzo[*e*]pyrene (xylene)[38]
34.	$AgClO_4\cdot$methylpyrene (from toluene)[6]
One-dimensional polymeric complexes	
Double-layer	
35.	$AgClO_4\cdot$acenaphthene[39]
36.	$AgClO_4\cdot$benzodioxan[40]
37.	$AgClO_4\cdot$benzo[*a*]triphenylene[41]
38.	$AgClO_4\cdot$diphenyloctatetraene[42]
39.	$AgClO_4\cdot$methylpyrene (from benzene)[43]
40.	$AgClO_4\cdot$methylbenzo[*a*]pyrene[38]
41.	$AgClO_4\cdot$benzo[*ghi*]perylene[11]
42.	$AgClO_4\cdot$triphenylene[9]
Triple-layer	
43.	$AgClO_4\cdot$coronene[34]
44.	$AgClO_4\cdot$dimethylanthracene[9]
Multi-layer	
45.	$AgClO_4\cdot$decacyclene (phenylene)[11]
46.	$AgClO_4\cdot$bifluorenylidene[9]
Slipped double-layer	
47.	$AgClO_4\cdot$benzo[*a*]pyrene (toluene)[34]
W-Type	
48.	$AgClO_4\cdot$benzene[44]
49.	$AgN(SO_2F)_2\cdot$benzene[45]
50.	AgOTf$\cdot$1,1,4,4-tetraphenylbutadiene[29]
51.	$AgClO_4\cdot$dibenz[*a*,*h*]anthracene[46]
52.	$AgClO_4\cdot$pyrene[10]
Inverting single-layer	
53.	$Ag(B_{11}CH_5Cl_6)\cdot$*p*-xylene[47]
54.	AgOTf$\cdot$*Z*-1,2-di-*tert*-butyl-1,2-diphenylethene[48]
55.	$Ag(B_9CH_4Br_5)\cdot$toluene[49]
56.	$Ag(B_9CBr_9)\cdot$benzene[50]
57.	$Ag(B_{11}CH_{11})\cdot$benzene[51]
Miscellaneous	
58.	$Ag(B_{11}C_2H_4Br_{10})\cdot$*p*-xylene[52]
59.	AgOTf$\cdot$dimethyldiphenyltetracyclododecene[5]
60.	AgOTf$\cdot$*Z*-1,2-(pentamethylphenyl)-1,2-diphenylethylene[5]
61.	$AgClO_4\cdot$1,1,4,4-tetraphenylbutadiene[29]
62.	$AgClO_4\cdot$benzo[*a*]phenathrene[46]
63.	$AgClO_4\cdot$anthracene[53]
64.	AgOTf$\cdot$hexaphenylbenzene[22]
65.	AgOTf$\cdot$benzene[54]
Two-dimensional polymeric complexes	
Cross-linked ML	
66.	$AgClO_4\cdot$benzophenanthrylene[55]
Cross-linked ISL	
67.	$AgClO_4\cdot$benzoanthracene[46]
Cross-linked W-type/SDL	
68.	$AgClO_4\cdot$perylene[10]
69.	$AgClO_4\cdot$fluoranthene[11]
Herringbone	
70.	AgOTf$\cdot$dibenzo[*b*,*def*]chrysene (toluene)[38]
71.	AgOTf$\cdot$naphtho(2,3-*a*)pyrene[46]
Pillared brick	
72.	$AgClO_4\cdot$[2.2]paracyclophane[11]
73.	$AgGaCl_4\cdot$[2.2]paracyclophane[56]
74.	$AgClO_4\cdot$triptycene[9]
Miscellaneous	
75.	$AgClO_4\cdot$tetraphenylethylene[29]
76.	AgOTf$\cdot$tetraphenylethylene[29]
77.	$AgClO_4\cdot$hexaphenylbenzene[57]
78.	AgOTf$\cdot$diphenylanthracene[9]
Three-dimensional polymeric complexes	
Miscellaneous	
79.	$AgClO_4\cdot$benzocyclooctatetraene[58]
80.	$AgClO_4\cdot$rubrene[34]

[a] L_1 = cobalt(III) bis(dicarbollide). [b] $L_2 = [\{((SiMe_3)_3C)_2Al_2F_5\}_2Li]$.

X-ray crystallographic analysis revealed a highly symmetric orthorhombic space group (*Pbam*) with one unique silver atom, half of a corannulene molecule, and one unique perchlorate anion in the asymmetric unit (Fig. 5). The corannulene moiety sits across a crystallographic mirror plane. Each corannulene moiety is coordinated to two silver atoms through neighboring rim bonds. There is very little perturbation of the corannulene skeleton upon silver complexation; the distance between carbon atoms coordinated to the silver atom is 1.378(11) Å, which is statistically the same as the rim bonds in the parent (1.380(9) Å).[7] The coordination sphere of each silver atom is tetrahedral, comprised of two η^2-corannulene ligands and two oxygen atoms from two different perchlorate counterions. The silver atom sits 2.32 Å above the mean plane of the benzenoid ring (*d*) with a deviation from the centroid axis of $\Delta = 1.67$ Å, which places it just outside the rim of corannulene and results in $\beta = 35.8°$. The angle between benzenoid planes (α) falls into the third range, $\alpha = 153°$. With the exception of the deviation from the benzenoid plane (*d*), these values are within the optimal ranges observed by Kochi (*cf.* Fig. 1),[5] although even *d* is close to the expected range.

An examination of the long-range structure of **2** reveals a 1-D polymer of corannulene dimers with two silver atoms connecting each corannulene bowl and perchlorate counterions bridging sandwich units. The bowls are stacked hub pointing to hub approximately 3.5 Å apart at the point of closest contact forming an open-faced sandwich motif. The basic connectivity is that of a double-layer array, with the exception that the corannulene units are not directly stacked above one another (Fig. 6). These 1-D polymeric arrays are packed in a zigzag pattern (Fig. 7) with a distance between similarly oriented polymers of ~7.2 Å.

Corannulene·silver(I) triflate complex (3)

A co-crystal containing silver(I) triflate and **1** was grown under degassed and dark conditions from a 1 : 1 mixture of $Ag(O_3SCF_3)–C_{20}H_{10}$ in toluene by slow vapor diffusion of

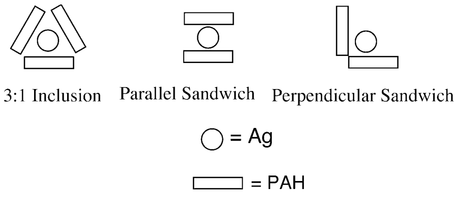

Fig. 2 Typical discrete complexes.

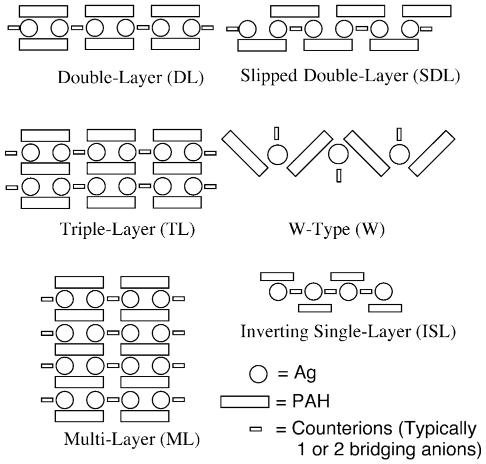

Fig. 3 Typical 1-D polymeric arrays.

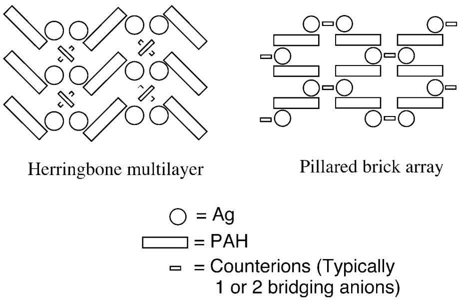

Fig. 4 Pillared brick and herringbone arrays.

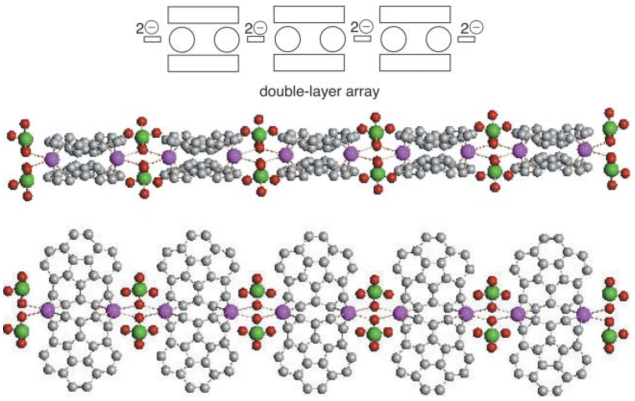

Fig. 6 Double-layer array of corannulene and silver perchlorate in **2** (viewed from two different directions).

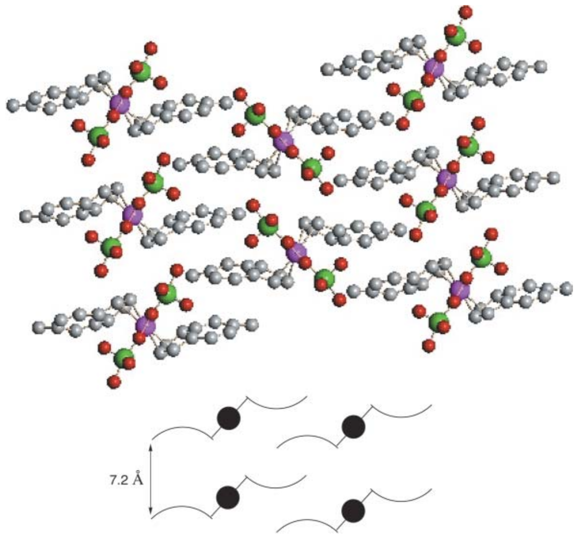

Fig. 7 Packing of **2**.

hexanes. A single crystal X-ray crystallographic analysis revealed a monoclinic unit cell ($P2_1/n$) with two unique silver atoms, two unique corannulene ligands, and two unique triflate anions (Fig. 8). Similar to the crystal with perchlorate counterions, one corannulene ligand is coordinated to two silver atoms through neighboring rim bonds. In contrast, the second corannulene ligand is coordinated to two silver atoms through the 1,2- and 5,6-positions (C_1–C_2 and C_7–C_8; Fig. 8). No statistically relevant deviation in the corannulene C–C bond lengths was observed.[7] The coordination sphere of each silver atom contains two η^2-corannulene ligands and two oxygen atoms from two different triflate counterions in a distorted tetrahedral environment. The location of each silver atom relative to the ligated benzenoid planes expressed in terms of d, Δ, β, and α can be found in Table 2. The bold entries indicate the most significant deviation from the optimal ranges observed by Kochi.[5]

An examination of the long-range structure of **3** reveals a 2-D grid of -(silver1–corannulene1–silver2–corannulene2)- polymers cross-linked *via* triflate ligands resulting in the basic connectivity of a slipped double-layer array (Fig. 9). A side-on view of the

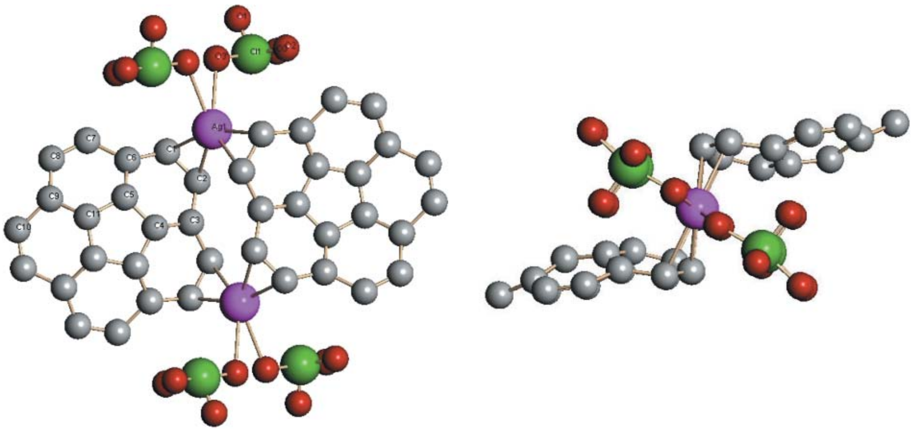

Fig. 5 Different views of the dimeric unit within the crystal structure of **2**.

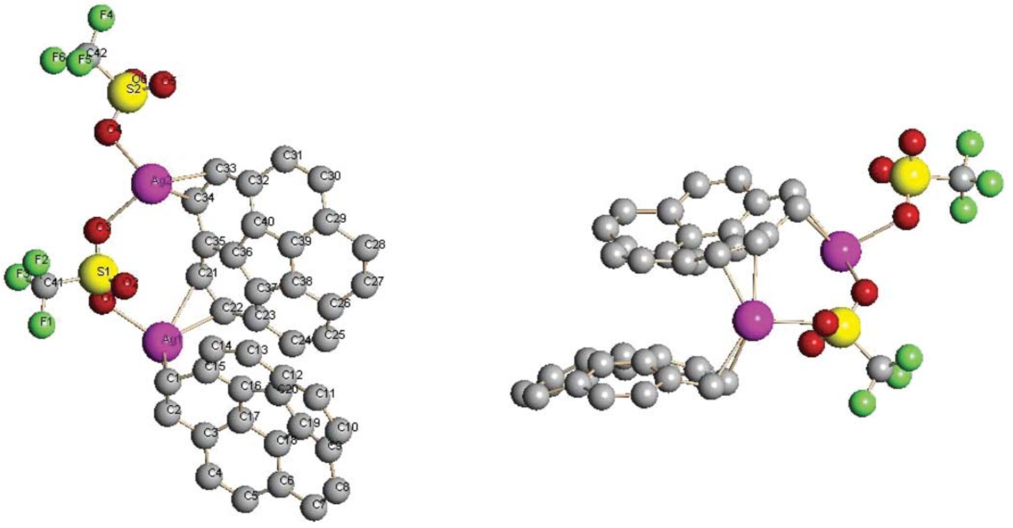

Fig. 8 Different views of the asymmetric unit of the crystal structure of **3**.

Table 2 The location of each silver atom in **3** relative to the ligated benzenoid planes expressed in terms of d, Δ, β, and α [a]

	Bond	d/Å	β/°	Δ/Å	α/°
Ag1	η^2 C21–C22	2.39	33.9	1.61	—
Ag1	η^2 C1–C2	**2.35**	35.2	1.66	**144**
Ag2	η^2 C7–C8	**2.31**	**38.4**	**1.83**	—
Ag2	η^2 C33–C34	2.39	31.0	1.44	**146**
Kochi standards		2.41 ± 0.05	32 ± 3	1.53 ± 0.2	130 or 155 ± 3

[a] Bold type indicates that the value is $>\sigma$ from the Kochi standard value.

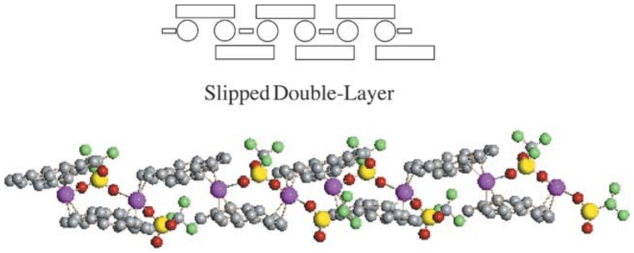

Fig. 9 SDL polymeric unit of complex **3**.

2-D sheets reveals a sinusoidal relationship between cross-linked polymers (Fig. 10). The sheets are stacked one atop another with a distance between sheets of ~3.5 Å (Fig. 11).

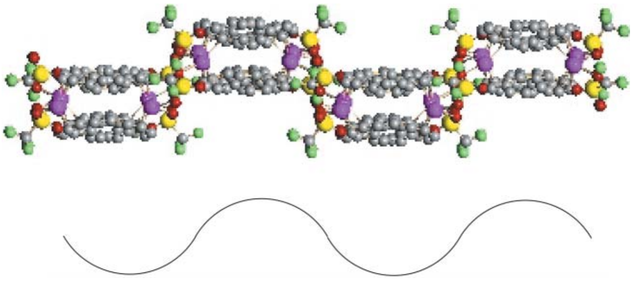

Fig. 10 Sinusoidal orientation of 2-D sheets in **3**.

Corannulene·silver(I) tetrafluoroborate complex (4)

A co-crystal containing silver(I) tetrafluoroborate and **1** was grown from a 1 : 1 mixture of Ag(BF$_4$)–C$_{20}$H$_{10}$ in toluene by slow vapor diffusion of hexanes. The crystals were grown in the absence of light in a nitrogen-containing glove box. These crystals were less stable than either the AgClO$_4$ or Ag(O$_3$SCF$_3$) co-crystals. Thus, additional care was required in their isolation and crystal structure determination. A single crystal X-ray crystallographic analysis revealed a triclinic unit cell ($P\bar{1}$) with two unique silver cations and two unique tetrafluoroborate anions, but only one unique corannulene moiety (Fig. 12). Three of the F atoms in one BF$_4^-$ anion are disordered over two orientations which are related by a pivot of approximately 30° about the fourth B–F bond. The corannulene ligand is coordinated to four silver atoms through four of the five rim bonds. Three of these contacts can be described as η^2-bonds and the fourth as an η^1-bond. Similar to the above discussion, no statistically relevant deviation in the corannulene C–C bond lengths was observed as a consequence of the coordination.[7] The coordination sphere of the first silver cation contains one η^2-corannulene ligand, one η^1-corannulene ligand and two fluorine atoms from two different tetrafluoroborate counterions. In contrast, the coordination sphere of the second silver cation contains two η^2-corannulene ligands and two fluorine atoms

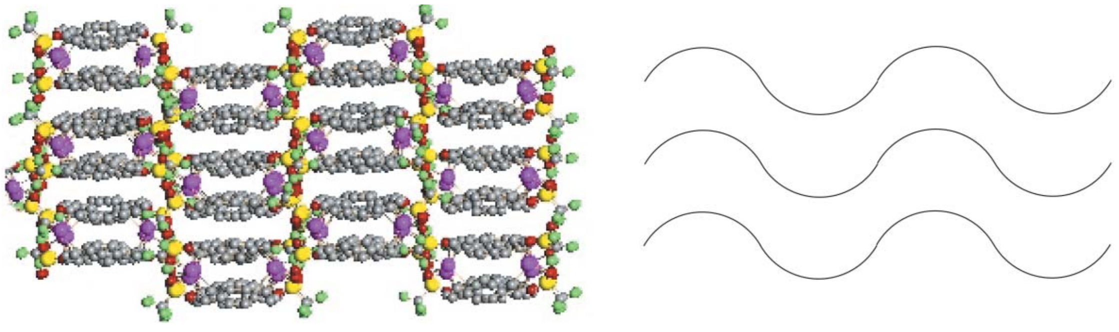

Fig. 11 Packing of sheets in **3**.

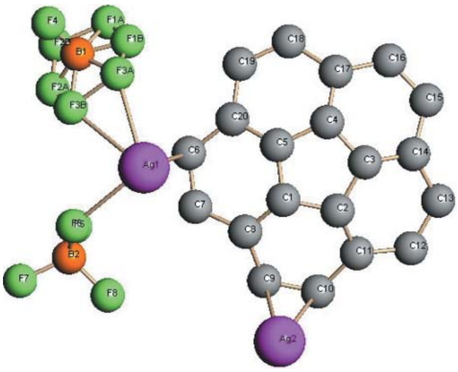

Fig. 12 The asymmetric unit in the structure of **4**.

Table 3 The location of each silver atom in **4** relative to the ligated benzenoid planes expressed in terms of d, Δ, β, and α [a]

	Bond	d/Å	β/°	Δ/Å	α/°
Ag1	η^2 C15–C16	2.43	34.7	1.69	—
Ag1	η^1 C6	**2.53**	34.9	**1.77**	**142**
Ag2	η^2 C9–C10	2.40	**36.5**	1.70	—
Ag2	η^2 C12–C13	**2.30**	35.7	1.65	156
Kochi standards		2.41 ± 0.05	32 ± 3	1.53 ± 0.2	130 or 155 ± 3

[a] Bold type indicates that the value is $>\sigma$ from the Kochi standard value.

from two different tetrafluoroborate couterions. The location of each silver atom relative to the ligated benzenoid planes expressed in terms of d, Δ, β, and α can be found in Table 3. The bold entries indicate the most significant deviation from the optimal ranges observed by Kochi.[5]

An examination of the long-range structure of **4** reveals a 2-D "cross-linked" grid. The basic connectivity in one dimension is that of a slipped double-layer array (Fig. 13). The connectivity in the other dimension, however, is that of a standard double-layer array (Fig. 14). The sheets are packed into a pattern reminiscent of a brick-wall, with the corannulene bowls of one sheet hovering over the tetrafloroborate units of the sheet below (Fig. 15).

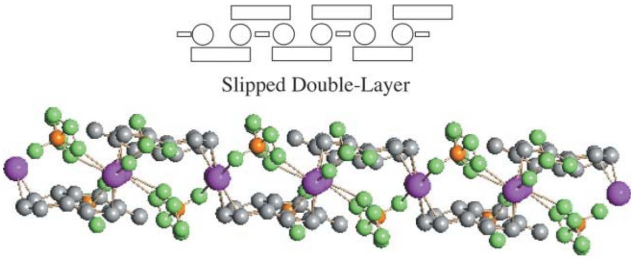

Fig. 13 SDL polymeric unit of complex **4**.

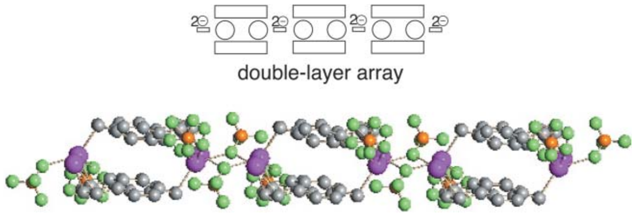

Fig. 14 DL polymeric unit of complex **4**.

Discussion

Comparison of silver complexes **2–4** reveals that silver has a tendency to form σ-donor-complexes with the rim bonds of corannulene. All the ligated silver atoms sit outside the rim (Δ range = 1.44–1.83 Å; mean 1.61 ± 0.13 Å) with a deviation from the benzene centroid axis (β) between 31.0° and 38.4° (34 ± 2°) and a normal distance to the benzenoid plane (d) of between 2.30 Å and 2.53 Å (2.38 ± 0.06 Å). As mentioned previously, a number of these parameters fall somewhat outside the optimal ranges observed by Kochi.[5] To understand these deviations, a model was developed to interpret the "ideal" versions of an η^1- or η^2-bond in terms of the Kochi parameters. In this model an ideal η^1- or η^2-bond is established when the silver atom is directly over the bonding orbitals of the arene ligand. If one assumes that the effective thickness of an aromatic plane is 3.4 Å (1.7 Å on either side)[8] and the atomic radius of silver(I) is 1.15 Å,[8] then the largest meaningful silver–arene interaction should be less than 2.85 Å. Furthermore, if one uses a regular hexagon with 1.4 Å sides as a model for benzene, then the "ideal" η^1- and η^2-bonds have the following geometric parameters: $\eta^1 \rightarrow \Delta = 1.4$ Å, $d \leq 2.85$ Å, $\beta \geq 26.2°$; $\eta^2 \rightarrow \Delta = 1.21$ Å, $d \leq 2.76$ Å, $\beta \geq 23.7°$. The interdependency of these parameters is worth noting. Of the parameters d, Δ, and β, only two are independent ($\Delta = d \tan\beta$). Analyzing the Kochi parameters in light of this model reveals that the optimum silver–monobenzenoid geometry places the silver atoms outside the arene ring ($\Delta = 1.5 \pm 0.2$ Å). It stands to reason that as Δ increases, $d_{\max}$ must decrease if the degree of orbital overlap and hence bond energy is to be maintained. Both of these perturbations will result in an increase in β. An examination of structures **2–4** reveals that this basic trend is observed.

One possible explanation for the deviation from optimal silver geometry in corannulene systems may be simply the result of the increased size of corannulene relative to monobenzenoid ligands. The increased size of a larger PAH ligand could force the bridging counter ions, and thus the silver atom, further away from the arene ring. This should lead to an overall increase in the length of Δ (and thus a decrease in d and increase in β). An examination of all reported silver complexes with PAH ligands, naphthlene or larger, lends support to this hypothesis.[4] This subset shows the following geometric parameters: $\Delta = 1.61 \pm 0.3$ Å, $d = 2.36 \pm 0.08$ Å and $\beta = 34 \pm 5°$. Additionally, a variety of structures exist where any one of these parameters

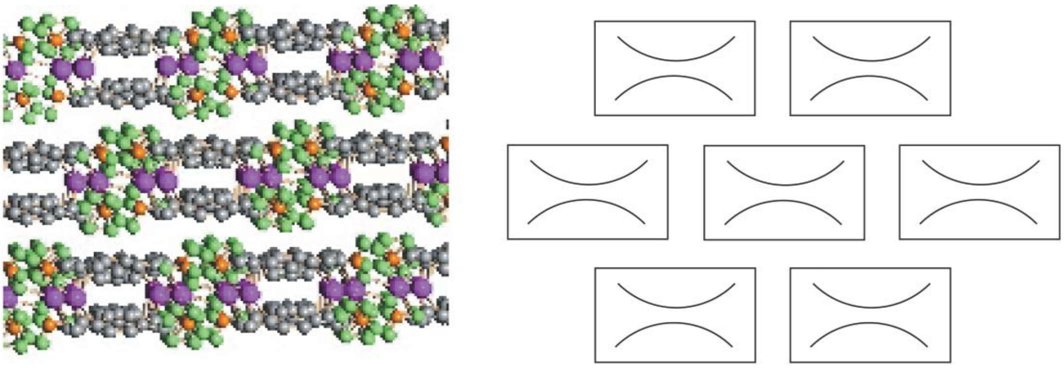

Fig. 15 Brick-like stacking of **4**.

are two to three σ away from the mean. Although these values are not statistically different from the Kochi parameters, they do suggest a slight shifting of the means. On average, silver complexation to larger PAHs results in a lengthening of Δ with a concomitant change in d and β. It is also of note that the parameter a was found to be an extremely flexible parameter. Values of a were discovered ranging from 91.5° to 168° with no apparent statistically relevant grouping. Thus it is reasonable to suggest that larger PAHs simply require more space and result in variations in the optimal geometric parameters.

A comparison of the long-range relationships present in complexes **2–4** reveals a number of similarities. All four complexes contain fragments reminiscent of 2 : 1 sandwiches. The basic dimeric units are then propagated as polymers with the basic connectivity of a double-layer or slipped double-layer array. Complexes **3** and **4** are further cross-linked into 2-D grids.

It is interesting to note, however, the drastic effect that simple variation of the counterion has on the overall structures. Complex **2** forms a simple 1-D polymer with double-layer connectivity. These polymers are then packed into a zigzag pattern in such a way as to minimize free space. Complexes **3** and **4** form 2-D grids, but the basic connectivity is different in each case. Furthermore, **4** forms a nearly "planar" sheet with each sheet packed one atop another. Complex **3**, on the other hand, is comprised of wave-like sheets, with each sheet stacked directly atop one another. Such changes in the long-range connectivity and crystal packing upon variation of silver counterion is a common occurrence and has been observed with ligands such as benzene, toluene, xylene, hexaphenylbenzene, tetraphenylethylene, 1,1,4,4-tetraphenylbutadiene, [2.2]paracyclophane and [2.2.2]paracyclophane (Table 1). Interestingly, simple variation of solvent can also affect long-range connectivity. Co-crystalization of $AgClO_4$ and 1-methylpyrene from benzene yields a 1-D double-layer polymer, while switching the solvent to toluene produces a discrete tetramer.[9]

It has been suggested that σ- and π-complexes of silver(I) with organic arene donors have the desired structural diversity for the construction of solid-state organometallic devices such as electrical conductors, photoactive switches, and chemical sensors.[5,10,11] Critical to this field of crystal engineering is the spontaneous self-assembly of active silver(I) centers within a defined environment.[5] The great variability in the packing of these silver–arene complexes, and the subtle ways in which it arises, impacts on the utility of silver–arene complexes in the rational design of devices and highlights the need for such systematic, albeit highly empirical, investigations. The appropriate variation of the crystallization conditions remains an art. Given that slight changes in complex composition or simply solvent variation can cause drastic changes in the basic connectivity of the resulting product, then rational design of polymeric systems can only be accomplished after the basic controlling principles have been elucidated.

Experimental

General methods

All manipulations were carried out under an inert atmosphere (either nitrogen or argon). All chemicals were reagent grade and used as received without further purification. Solvents were dried and distilled by standard methods before use. Solvents that were taken into the dry box were further degassed by standard freeze–pump–thaw techniques. Silver salts were obtained from Aldrich. Corannulene was synthesized following the literature procedure.[12] The crystal diffraction data for **2** and **3** was collected on a *Bruker P4* diffractometer, while that for **4** was collected on a *Nonius KappaCCD* area-detector diffractometer.

CCDC reference numbers 246840–246842 for compounds **2–4**. See http://www.rsc.org/suppdata/ob/b4/b411987h/ for crystallographic data in .cif or other electronic format.

$[Ag(C_{20}H_{10})]ClO_4$ (2)

An oven-dried 7 mL test tube and 33 mL screw-cap vial were cooled under a constant stream of argon gas. Corannulene (**1**) (10.1 mg, 0.04 mmol), silver(I) perchlorate (8.1 mg, 0.04 mmol) and toluene (2 mL) were added to the test tube and hexane (10 mL) was added to the outer vial. The vial was quickly capped, and wrapped tightly with parafilm and aluminum foil. After 4 days bright yellow crystals were obtained.

Crystal data for compound **2**: $C_{20}H_{10}AgClO_4$, $M_r = 457.60$, orthorhombic, space group *Pbam*, $a = 20.362(2)$, $b = 7.229(1)$, $c = 10.289(1)$ Å, $V = 1514.5(4)$ Å^{-3}, $Z = 4$, $D_x = 2.077$ g cm^{-3}, $T = -98$ °C, *Bruker P4* diffractometer, Mo Kα radiation, $\lambda = 0.71073$ Å, $\mu = 1.533$ mm^{-1}, $\theta_{max} = 30°$, 2733 measured reflections, 2102 symmetry-independent reflections, 1542 reflections with $I > 2\sigma$ (I), no absorption correction, refinement with *SHELXL-97* on F^2, 132 parameters, $R(F)$ $[I > 2\sigma(I)$ reflections$] = 0.060$, $wR(F^2)$ [all reflections] $= 0.163$, $S = 1.067$, $\Delta\rho_{max} = 2.06$ e Å^{-3}. Two equally occupied positions were refined for one O atom of the perchlorate anion to account for disorder.

$[Ag(C_{20}H_{10})](O_3SCF_3)$ (3)

An oven dried 7 mL test tube and 33 mL screw-cap vial were cooled under a constant stream of argon gas. Corannulene (**1**) (21.1 mg, 0.084 mmol), silver(I) triflate (21.4 mg, 0.083 mmol) and toluene (2 mL) were added to the test tube and hexane (10 mL) was added to the outer vial. The vial was quickly capped, and wrapped tightly with parafilm and aluminum foil. After 4 days bright yellow crystals were obtained.

Crystal data for compound **3**: $C_{42}H_{20}Ag_2F_6O_6S_2$, $M_r = 1014.4$, monoclinic, space group $P2_1/c$, $a = 12.690(2)$, $b = 22.206(2)$, $c = 12.898(2)$ Å, $\beta = 107.637(8)°$, $V = 3463.7(7)$ Å^{-3}, $Z = 4$, $D_x = 1.945$ g cm^{-3}, $T = -100$ °C, *Bruker P4* diffractometer, Mo Kα radiation, $\lambda = 0.71073$ Å, $\mu = 1.338$ mm^{-1}, $\theta_{max} = 25°$, 6368 measured reflections, 6080 symmetry-independent reflections, 5221 reflections with $I > 2\sigma$ (I), no absorption correction, refinement with *SHELXL-97* on F^2, 523 parameters, $R(F)$ $[I > 2\sigma(I)$ reflections$] = 0.050$, $wR(F^2)$ [all reflections] $= 0.161$, $S = 1.080$, $\Delta\rho_{max} = 0.80$ e Å^{-3}.

$[Ag_2(C_{20}H_{10})](BF_4)_2$ (4)

An oven-dried 4 mL vial and 11 mL screw-cap vial were taken into a nitrogen atmosphere glove box. Corannulene (**1**) (10.1 mg, 0.04 mmol), silver(I) tetrafluoroborate (9.1 mg, 0.047 mmol) and toluene (1 mL) were added to the inner vial and hexane (5 mL) was added to the outer vial. The outer vial was capped and stored away from light. After 4 days bright yellow crystals were obtained.

Crystal data for compound **4**: $C_{20}H_{10}Ag_2B_2F_8$, $M_r = 639.64$, triclinic, space group $P\bar{1}$, $a = 9.5741(2)$, $b = 9.6621(2)$, $c = 10.6735(2)$ Å, $\alpha = 98.304(1)$, $\beta = 110.3937(1)$, $\gamma = 101.4884(9)°$, $V = 882.01(3)$ Å^{-3}, $Z = 2$, $D_x = 2.408$ g cm^{-3}, $T = -113$ °C, *Nonius KappaCCD* area-detector diffractometer, Mo Kα radiation, $\lambda = 0.71073$ Å, $\mu = 2.309$ mm^{-1}, $\theta_{max} = 30°$, 24787 measured reflections, 5144 symmetry-independent reflections, 4337 reflections with $I > 2\sigma$ (I), absorption correction based on analysis of equivalent reflections (*SORTAV*), refinement with *SHELXL-97* on F^2, 318 parameters, $R(F)$ $[I > 2\sigma(I)$ reflections$] = 0.030$, $wR(F^2)$ [all reflections] $= 0.075$, $S = 1.025$, $\Delta\rho_{max} = 1.07$ e Å^{-3}, secondary extinction coefficient = 0.0048(5). Three of the F atoms in one BF_4^- anion are disordered over two orientations which are related by a pivot of approximately 30° about the fourth B–F bond. Two sets of positions were defined for these F atoms and the site occupation factor of the major conformation refined to 0.643(5).

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