Variable Ag(I) Coordination Modes in Silver Cobalt(III) Bis(dicarbollide) Supramolecular Assemblies with Cyclotriveratrylene Host Molecules

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ABSTRACT: The crystal structure of the silver complex $Ag(CH_3CN)_2[Co(C_2B_9H_{11})_2]$ has been determined and features trigonal bipyramidal Ag(I) with B−H···Ag interactions comprising the trigonal plane. When the host molecule cyclotriveratrylene (CTV) is combined with silver(I) cobalt(III) bis(dicarbollide), different supramolecular assemblies with various Ag(I) coordination environments result, depending on the crystallization conditions used. The complex $Ag(CH_3CN)(H_2O)(CTV)_2[Co(C_2B_9H_{11})_2]$ has tetrahedral Ag(I) with coordination interactions with water, acetonitrile, and CTV through Ag−C bonds, and the structure features bis(CTV) capsules. The complexes $Ag(CH_3CN)_3(CTV)$-$[Co(C_2B_9H_{11})_2](CH_3CN)_{0.5}$ and $Ag(CH_3CN)_4(CTV)[Co(C_2B_9H_{11})_2](CH_3CN)_{0.25}$ both have $[Ag(CH_3CN)_n]^+$ complex cations forming host−guest interactions with the CTV. In the former case, three CH_3CN ligands bind to Ag(I) and there are further weak Ag−O coordinate interactions to the CTV, whereas the latter features the more usual tetrahedral $[Ag(CH_3CN)_4]^+$. Complexes with CTV show host−guest interactions with coordinated acetonitrile guests.

Introduction

The sandwich complex cobalt(III) bis(dicarbollide) and its derivatives are weakly coordinating anions,[1] with applications in catalysis[2] and in the extraction of radionuclides from nuclear waste.[3] The use of cobalt-(III) bis(dicarbollide) as an anion in supramolecular chemistry is in its infancy, and examples include cobalt-(III) bis(dicarbollide) as a counterion for coordination polymers,[4,5] coordinate chains involving Ag···H−B interactions,[6] and as a counterion in host−guest complexes with a curved Ni macrocycle[7] and cyclotriveratrylene,[8] where hydrogen bonding interactions from the acidic cobalt(III) bis(dicarbollide) C−H groups may be observed.
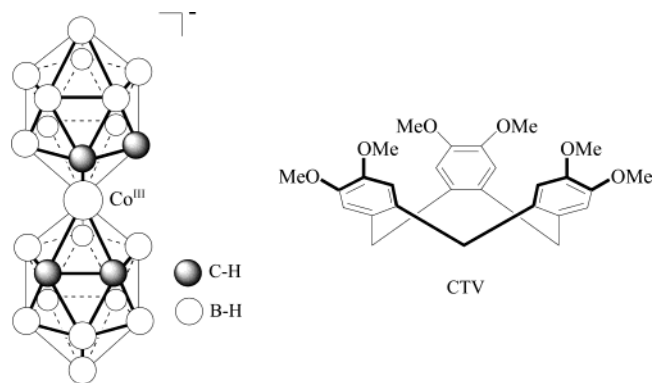
The host molecule cyclotriveratrylene (CTV) has a relatively rigid bowl shape, creating a molecular cavity, much like those seen in cone conformation calixarenes.[9] The host−guest chemistry of CTV is, however, quite distinct from that of the calixarenes. CTV forms ball-and-socket type supermolecules with large neutral and cationic guest molecules such as 1,2-dicarbadodecarbo-

rane,[10,11] fullerene-C_{60},[12] $[FeCp(C_6H_5R)]^+$,[13] and {Na-[2.2.2]cryptate}$^+$,[8] however tends to form clathrate materials with small guest molecules, where the CTV molecules stack on top of one another and the guest molecules are contained in channels created by the packing of pillars of CTV molecules.[14] One example of a γ-phase is known where acetone is complexed between two CTV molecules forming a capsule-like dimer.[15] More recently, small organic solvent molecules have been complexed within the CTV molecular cavity when CTV forms part of a coordinate or hydrogen bonded network structure.[5,11,16,17] CTV has also proved to be a valuable building-block for the synthesis of more sophisticated host molecules such as cryptophanes and extended arm cavitands, where intracavity complexation of small and large guest molecules is common place.[18] CTV has been employed as a ligand, both in coordination complexes with Ag(I)[19] and group 1 metals[5,11,16] binding to the dimethoxy groups, and organometallic complexes with CTV as a π-type ligand.[20] In the latter case, the organometallic complex acts as a host for anions. Other examples of CTV coordination complexes involve extended arm CTV derivatives, where additional ligand functionality has been added covalently to the CTV backbone.[21]

We report herein a series of compounds involving complex and host−guest formation with $Ag[Co-(C_2B_9H_{11})_2]$, CTV, and acetonitrile. The coordination modes of the Ag(I) center changes dramatically across the series and includes organometallic coordination to CTV, an unusual five-coordinate $[Ag(CH_3CN)_3(CTV)]^+$ coordination complex, and the anticipated four-coordinate $[Ag(CH_3CN)_4]^+$. Which crystalline complex is isolated is dependent on the composition of the crystallization solvent. The structure obtained without addition of CTV was also studied, where a trigonal bipyramidal Ag(I) coordination sphere is observed, with B−H···Ag interactions forming the trigonal plane.

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Table 1. Details of X-ray Data Collection and Structure Refinement for 1−4

	1	2	3	4
formula	$C_8H_{26}AgB_{18}CoN_2$	$C_{60}H_{87}AgB_{18}CoNO_{13}$	$C_{38}H_{62.5}AgB_{18}CoN_{3.5}O_6$	$C_{39.5}H_{64.75}AgB_{18}CoN_{4.25}O_6$
M_r	511.69	1391.69	1024.28	1056.59
crystal color and shape	yellow-orange, prism	yellow-orange, multifaceted prism	yellow-orange, diamond-rectangular	yellow-orange, prism
crystal size (mm)	$0.15 \times 0.14 \times 0.13$	$0.30 \times 0.17 \times 0.17$	$0.17 \times 0.14 \times 0.13$	$0.20 \times 0.17 \times 0.10$
crystal system	monoclinic	monoclinic	triclinic	triclinic
space group	Cc	$C2/m$	$P\bar{1}$	$P\bar{1}$
T (K)	150(1)	150(1)	100(1)	100(1)
a (Å)	7.1475(2)	20.8368(2)	13.0734(1)	12.3042(1)
b (Å)	28.7276(10)	14.8687(2)	13.7200(2)	12.9172(1)
c (Å)	10.7856(4)	10.8352(1)	15.2873(2)	17.4093(2)
α (°)	90	90	81.817(1)	75.765(1)
β (°)	93.829(2)	99.651(4)	80.249(1)	85.195(1)
γ (°)	90	90	68.822(1)	85.813(1)
U (Å³)	2209.7(1)	3309.41(6)	2509.95(5)	2668.64(4)
Z	4	2	2	2
ρ_c (g cm^{-3})	1.538	1.397	1.357	1.315
$F(000)$	1008	1444	1054	1087
μ (cm^{-1})	1.636	0.61	0.767	0.724
2θ range (°)	2.36−28.28	1.69−27.48	2.10−27.50	2.26−27.53
no. data collected	11018	18897	38567	47266
no. unique data	5064	3913	11284	12126
R_{int}	0.092	0.059	0.0524	0.053
no. obs. data $(I > 2\sigma(I))$	4385	3728	9280	8245
no. parameters	280	235	631	640
no. restraints	2	0	0	0
R_1 (obs. data)	0.0404	0.1089	0.0405	0.0529
wR_2 (all data)	0.0934	0.2763	0.1181	0.1609
S	1.040	1.149	1.039	1.062
min, max residual electron density (e Å³)	−0.704, 0.493	−3.062, 0.689	−0.841, 0.842	−1.061, 1.018

Experimental Section

Cyclotriveratrylene[22] and Ag[Co(C$_2$B$_9$H$_{11}$)$_2$] [1] were prepared by literature methods. AR grade solvents were used without further purification.

Synthesis of Ag(CH$_3$CN)$_2$[Co(C$_2$B$_9$H$_{11}$)$_2$] (1). Ag[Co-(C$_2$B$_9$H$_{11}$)$_2$] was recrystallized from a 4:1 mixture of CH$_3$CN and CF$_3$CH$_2$OH and allowed to stand uncovered. Yellow-orange crystals of **1** were deposited after a day in 70% yield. Satisfactory microanalytical data could not be obtained, possibly due to loss of CH$_3$CN.

Synthesis of Ag(CH$_3$CN)(H$_2$O)(CTV)$_2$[Co(C$_2$B$_9$H$_{11}$)$_2$] (2). Ag[Co(C$_2$B$_9$H$_{11}$)$_2$] (5.2 mg, 12 μmol) was dissolved in CH$_3$CN and added to CTV (5.3 mg, 11.7 μmol) in CF$_3$CH$_2$OH, with CH$_3$-CN/CF$_3$CH$_2$OH in 3:7 proportions and the solution allowed to stand uncovered. Yellow-orange crystals of **2** appeared after several days in 56% yield. Microanalysis % found (calculated) C 51.85 (51.78); H 6.30 (6.30); N 1.10 (1.01).

Synthesis of Ag(CH$_3$CN)$_3$(CTV)[Co(C$_2$B$_9$H$_{11}$)$_2$](CH$_3$CN)$_{0.5}$ (3). Ag[Co(C$_2$B$_9$H$_{11}$)$_2$] (5.0 mg, 11.6 μmol) was dissolved in CH$_3$-CN and added to CTV (10.2 mg, 22.6 μmol) in CF$_3$CH$_2$OH, with CH$_3$CN/CF$_3$CH$_2$OH in 3:1 proportions and the solution allowed to stand uncovered. Yellow-orange crystals of **3** appeared after several days in 60% yield. Microanalysis % found (calculated) C 43.75 (44.50); H 5.85 (6.14); N 4.20 (4.78). A 1:1 mixture of Ag[Co(C$_2$B$_9$H$_{11}$)$_2$] and CTV gives the same product.

Synthesis of Ag(CH$_3$CN)$_4$(CTV)[Co(C$_2$B$_9$H$_{11}$)$_2$](CH$_3$CN)$_{0.25}$ (4). Ag[Co(C$_2$B$_9$H$_{11}$)$_2$] (4.7 mg, 10.9 μmol) and CTV (4.8 mg, 10.6 μmol) were dissolved separately in CH$_3$CN, mixed, and the solution allowed to stand uncovered. Yellow-orange crystals of **4** appeared after several hours. The crystals lost solvent and hence crystallinity on exposure to the atmosphere, which does not allow for meaningful yields or microanalysis.

X-ray Collections and Structure Determinations. Details of data collection and structure refinement for **1−4** are given in Table 1. Single crystals of **1−4** were mounted on a glass fiber under oil and X-ray data collected on a Nonius KappaCCD diffractometer at low temperatures with Mo Kα radiation ($\lambda = 0.71073$ Å). Data were corrected for Lorenztian and polarization effects but not absorption. The structures were solved by direct methods using SHELXS-97 and refined by full matrix least-squares on F^2 using SHELXL-97. All non-

hydrogen atoms were refined anisotropically and hydrogens included in geometrically estimated positions with a riding refinement unless otherwise indicated. C positions within carborane cages were determined by examining displacement parameters and bond lengths, noting that C−C bond lengths are considerably shorter than those for C−B or B−B. Complex **2** showed symmetry induced disorder with the two C positions within each carborane cage distributed over three vertexes, and two symmetry equivalent positions within the CH$_3$CN refined with half C and half N character. The Ag and O were refined at half occupancy due to a symmetry imposed disorder. Hydrogens were not included for H$_2$O or CH$_3$CN. A solvent CH$_3$CN molecule was refined at half occupancy in **3**, and shows symmetry induced disorder. Hydrogens were not included for this CH$_3$CN. In complex **4**, a partially occupied CH$_3$CN molecule is disordered across an inversion center, and was refined isotropically and hydrogen positions for this CH$_3$CN were not included in the refinement.

Results and Discussion

Recrystallization of Ag[Co(C$_2$B$_9$H$_{11}$)$_2$] from a CH$_3$CN/CF$_3$CH$_2$OH solution gives the complex Ag(CH$_3$CN)$_2$[Co-(C$_2$B$_9$H$_{11}$)$_2$] **1** with roughly linear coordination of CH$_3$CN ligands to the Ag$^+$ center. The structure is described more fully below. Slow evaporation of solutions of CTV and Ag[Co(C$_2$B$_9$H$_{11}$)$_2$] in mixed CH$_3$CN/CF$_3$CH$_2$OH solvent systems gives two distinct crystalline materials, Ag(CH$_3$CN)(H$_2$O)(CTV)$_2$[Co(C$_2$B$_9$H$_{11}$)$_2$] **2** and Ag(CH$_3$-CN)$_3$(CTV)[Co(C$_2$B$_9$H$_{11}$)$_2$](CH$_3$CN)$_{0.5}$ **3**. Slow evaporation of a neat CH$_3$CN solution containing CTV and Ag[Co(C$_2$B$_9$H$_{11}$)$_2$] gives the crystalline complex Ag(CH$_3$-CN)$_4$(CTV)[Co(C$_2$B$_9$H$_{11}$)$_2$](CH$_3$CN)$_{0.25}$ **4**. The number of CH$_3$CN molecules that coordinate to the Ag$^+$ center increases from one for **2**, three for **3**, and four for **4**, and the structures are described more fully below. Complexes **2−4** are not polymorphs as they have slightly different compositions, and represent a system where the composition of the crystallizing solvent determines

Table 2. Selected Bond Lengths and Angles for 1−4[a]

Complex **1**[b]			
Ag(1)−N(1)	2.143(4)	N(1)−Ag(1)−N(2)	167.26(16)
Ag(1)−N(2)	2.154(4)	H(2)−Ag(1)−H(11)	68.13
Ag(1)−H(2)	2.352	H(2)−Ag(1)−H(5)I	143.33
Ag(1)−H(5)I	2.561	H(11)−Ag(1)−H(5)I	145.91
Ag(1)−H(11)	2.400	N(1)−Ag(1)−H(2)	89.40
Ag(1)···B(2)	3.296	N(1)−Ag(1)−H(11)	95.93
Ag(1)···B(5)I	3.222	N(1)−Ag(1)−H(5)I	96.78
Ag(1)···B(11)	3.337	N(2)−Ag(1)−H(2)	101.97
		N(2)−Ag(1)−H(11)	83.21
		N(2)−Ag(1)−H(5)I	77.58
Complex **2**			
Ag(1)−CN(1)	2.038(13)	CN(1)−Ag(1)−O(4)	125.6(5)
Ag(1)−O(4)	2.369(15)	CN(1)−Ag(1)−C(5)	125.6(2)
Ag(1)−C(5)	2.607(7)	O(4)−Ag(1)−C(5)	91.7(3)
Ag(1)−C(5)II	2.607(7)	C(5)−Ag(1)−C(5)II	84.8(3)
CN(1)−C(15)	1.313(13)		
Complex **3**			
Ag(1)−N(1)	2.206(2)	N(1)−Ag(1)−N(2)	104.09(8)
Ag(1)−N(2)	2.466(2)	N(1)−Ag(1)−N(3)	157.52(9)
Ag(1)−N(3)	2.184(2)	N(2)−Ag(1)−N(3)	95.79(9)
Ag(1)−O(3)	2.685(2)	O(3)−Ag(1)−O(4)	55.61(5)
Ag(1)−O(4)	2.834(2)	O(3)−Ag(1)−N(1)	89.48(7)
		O(3)−Ag(1)−N(2)	85.77(7)
		O(3)−Ag(1)−N(3)	102.52(8)
		O(4)−Ag(1)−N(1)	77.65(7)
		O(4)−Ag(1)−N(2)	141.37(7)
		O(4)−Ag(1)−N(3)	93.38(8)
Complex **4**			
Ag(1)−N(1)	2.303(3)	N(1)−Ag(1)−N(2)	100.93(12)
Ag(1)−N(2)	2.292(4)	N(1)−Ag(1)−N(3)	101.03(14)
Ag(1)−N(3)	2.297(5)	N(1)−Ag(1)−N(4)	118.60(13)
Ag(1)−N(4)	2.226(3)	N(2)−Ag(1)−N(3)	99.47(14)
		N(2)−Ag(1)−N(4)	120.72(14)
		N(3)−Ag(1)−N(4)	112.75(13)

[a] Symmetry codes I: x, $-y$, $0.5 + z$; II: x, $1 - y$, z. [b] Hydrogen atoms at calculated positions.
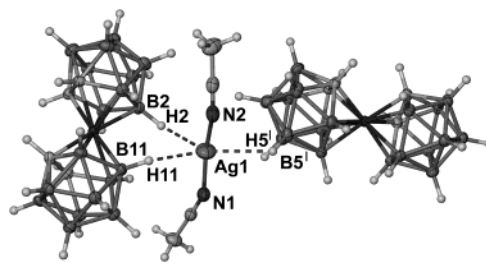

Figure 1. Coordination environment of silver center in **1**. Weak B−H···Ag interactions shown as dashed lines. Ellipsoids are shown at 50% probability level. I: x, $-y$, $0.5 + z$.
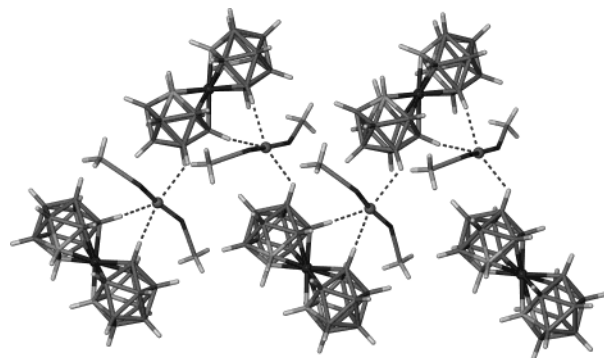

Figure 2. Coordinate chain in **1**.

the nature of the coordination complex isolated and subsequent host−guest characteristics.

2,2,2-Trifluoroethanol was used as it has been a successful crystallization solvent in related systems;[5] however, $Ag[Co(C_2B_9H_{11})_2]$ is insoluble in neat CF_3CH_2-OH. When the minimum amount of CH_3CN required to dissolve the $Ag[Co(C_2B_9H_{11})_2]$ was added, complex **2** was isolated. When a higher proportion of CH_3CN was used, typically, a 3:1 CH_3CN/CF_3CH_2OH mix, complex **3** was isolated. Attempts were made to determine the exact starting solvent composition that leads to the crystallization **2** or **3**; however, this was not successful, which is unsurprising given the crystals were grown by slow evaporation of solvent. This means that the actual composition of the solvent mix at the point of crystallization cannot be easily ascertained, and the nature of changes in solvent composition would be affected by small changes in ambient conditions. Complexes **2−4** have quite distinctive crystal habits (Table 1), and there was no indication of different species crystallizing within the same batch. Furthermore, the unit cell parameters of several crystals from each batch were checked and no discrepancies were observed.

$Ag(CH_3CN)_2[Co(C_2B_9H_{11})_2]$ 1. Complex **1** crystallizes in a monoclinic cell and the structure was solved in the chiral space group *Cc*. The asymmetric unit consists of a $[Co(C_2B_9H_{11})_2]^-$ anion and $[Ag(CH_3CN)_2]^+$ cation, both on general positions. Selected bond lengths and angles are given in Table 2.

The Ag(I) center is coordinated by two CH_3CN molecules arranged in a nearly linear fashion with a N(1)−

Ag(1)−N(2) angle of 167.26(16)°. The coordination sphere of the Ag(I) center is completed by weak interactions to B−H groups of the $[Co(C_2B_9H_{11})_2]^-$ anion, Figure 1. Two B−H hydrogen atoms from one $[Co(C_2B_9H_{11})_2]^-$, and one from a symmetry related $[Co(C_2B_9H_{11})_2]^-$ anion interact with the Ag^+ at B−H···Ag distances ranging from 2.35 to 2.56 Å, Table 2. B−H···Ag interactions are not uncommon for carborane anions although these distances are somewhat longer than those for most previously reported examples, where B−H···Ag distances are of the order 2−2.2 Å,[6,23,25] although a longer distance of 2.51(2) Å has recently been reported.[23] The long distances indicate that these interactions are weak. The geometry around the Ag^+ is distorted trigonal bipyramidal, with the three coordinating H atoms forming the equatorial plane. The Ag^+ is displaced by <0.5 Å from the center of the (H)$_3$ plane. Trigonal bipyramidal is not a common coordination environment for Ag(I), although a number of other examples have been reported,[26] most notably in this context the complex $Ag_2(CH_3CN)_3(2$-$B_{10}H_9F)$.[24] In $Ag_2(CH_3CN)_3(2$-$B_{10}H_9F)$ one of the Ag^+ centers is coordinated by three CH_3CN molecules in a slightly distorted trigonal plane, with B−H···Ag interactions in axial positions.

Each $[Co(C_2B_9H_{11})_2]^-$ anion in **1** coordinates to two Ag^+ centers through three B−H groups, and a stepped cation−anion coordinate chain is formed, Figure 2. A similar cation−anion coordinate chain is reported for $(\eta^2$-*p*-xylene$)Ag[Co(C_2B_9H_{11})_2]$, where each $[Co(C_2B_9H_{11})_2]^-$ anion also coordinates to two Ag^+ centers via three B−H···Ag interactions.[6] In the extended structure of **1**, the coordinate chains pack together with close contacts between the $[Co(C_2B_9H_{11})_2]^-$ anions. Each C−H group is in close contact with a B−H group from an adjacent chain (C−H···H−B distances 2.10−2.27 Å) consistent with the formation of dihydrogen bonds,[27]
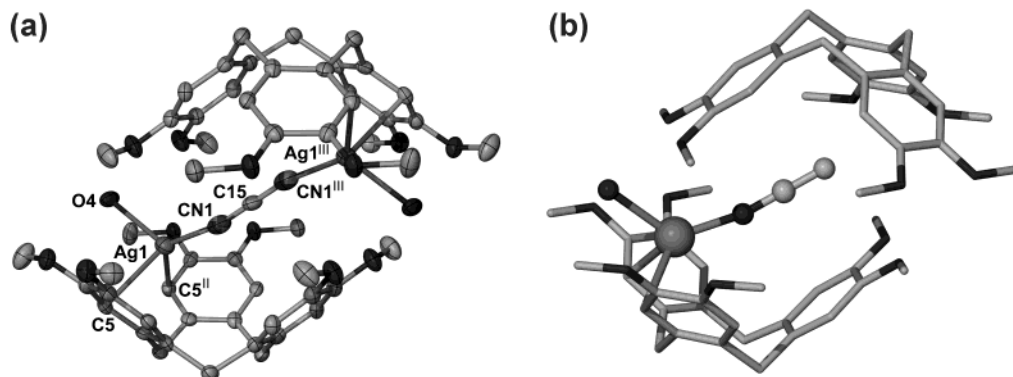
Figure 3. (a) Capsule assembly of **2**. The apparent bridging acetonitrile ligand is an artifact of disorder, and the Ag and H_2O positions shown are actually 50% occupied, see text and Figure 4. Ellipsoids are shown at 50% probability level. II: $x, 1 - y, z$, III $-x, y, -z$. (b) Ball-and-stick diagram showing one of the disordered positions, symmetry equivalent Ag and O positions have been omitted.

noting that hydrogen bond formation from the acidic C—H groups of carboranes is now well established.[28]

$Ag(CH_3CN)(H_2O)(CTV)_2[Co(C_2B_9H_{11})_2]$ 2. Complex **2** crystallizes in a monoclinic cell and the structure was solved in space group $C2/m$. The asymmetric unit consists of one-quarter of $[Co(C_2B_9H_{11})_2]^-$ anion, Ag^+, CH_3CN, and H_2O molecules and one-half of the CTV, with the Ag and CH_3CN positions on sites of m symmetry, and Co on a site of $2/m$ symmetry. The Ag-$(H_2O)(CH_3CN)$ moiety is disordered with the $Ag(H_2O)$ at 50% occupancy at each site and CH_3CN at 100% occupancy however with C/N disorder. Selected bond lengths and angles are given in Table 2.

The Ag(I) coordination sphere in **2** is four-coordinate with distorted tetrahedral geometry, Table 2. There is one aquo ligand at Ag—O distance 2.369(15) Å, an acetonitrile molecule at Ag—N 2.038(13) Å and Ag—C bonds to the C6 position of one veratrole ring within the CTV (Ag—C distance 2.607(7) Å) and to the symmetry equivalent C3 position of an adjacent ring. The Ag—C distance is marginally long compared with related Ag—arene systems.[6,25,29] Ag—arene coordinate interactions have been also reported for Ag complexes of related calixarene and calixresorcinarene host molecules.[25,29]

The Ag^+ cation is situated within the CTV molecular cavity. This is similar to what is observed in Ag^+ complexation by calixarenes; however, it is quite different to other examples of organometallic complexation of CTV. Other reported examples are of Rh, Ir, or Ru complexes where one, two, or three of the veratrole faces of the CTV act as a η^6 ligand to a metal center that located on the outside of the CTV.[20]

The aquo ligand in **2** is exo to the CTV cavity, while the acetonitrile ligand is inside the CTV cavity and points along the plane of the arene ring not involved in coordination to Ag. The acetonitrile molecule appears to bridge to another Ag^+ center coordinated to another CTV molecule to produce a capsule-like bis(CTV) dimer, Figure 3; however, the appearance of a bridging acetonitrile is an artifact of the symmetry induced disorder of the $Ag(H_2O)(CH_3CN)$ moiety. The bis(CTV) capsule actually comprises a $Ag(H_2O)(CH_3CN)(CTV)$ complex like that shown in Figure 3b and schematically in Figure 4, with a second molecule of CTV in an inverted orientation, associated with the first via host—guest interactions with the coordinated acetonitrile. This type
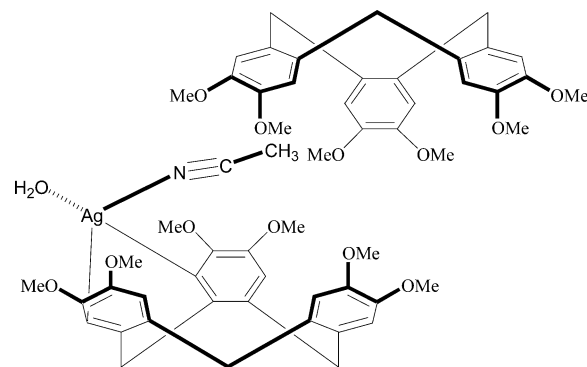

Figure 4. Schematic diagram of capsule assembly found in **2**. The Ag(I) center coordinates to one CTV molecule while the coordinated CH_3CN molecule acts as a guest for the other CTV. In the crystal structure, the two CTV molecules are crystallographically equivalent and the averaged, disordered structure shown in Figure 3a is obtained.

of building of secondary structure through host—guest interactions has been successfully exploited in calixarene systems by Hosseini and co-workers.[30] In the crystal structure of **2**, the two CTV molecules associated with each capsule are crystallographically equivalent. This means that for each capsule assembly, the position of the $Ag(H_2O)(CH_3CN)$ moiety is as shown in Figure 4 half the time, and half the time in the inverted orientation with the Ag^+ coordinating to the upper CTV of Figure 4. The positions of the CH_3CN atoms necessarily coincide for each orientation, and the CH_3CN is at full occupancy within the capsule, although with sites of mixed C/N character. The $Ag(H_2O)$ sites are at 50% occupancy.[31]

The extended structure for **2** is shown in Figure 5. The capsules stack in the c direction, possibly through a weak hydrogen bond between the coordinated aquo ligand and dimethoxy group of neighboring capsules (O···O separation 3.43 Å). Capsules that are adjacent in the bc plane associate through π—π interactions between arene rings of the CTV molecules where the centroid separation is 3.696 Å. The $[Co(C_2B_9H_{11})_2]^-$ anions are located in hydrophobic pockets and show no significant interactions with neighboring molecules.

$Ag(CH_3CN)_3(CTV)[Co(C_2B_9H_{11})_2](CH_3CN)_{0.5}$ 3. Complex **3** crystallizes in a triclinic cell and the structure was solved in space group $P\bar{1}$. The asymmetric unit of
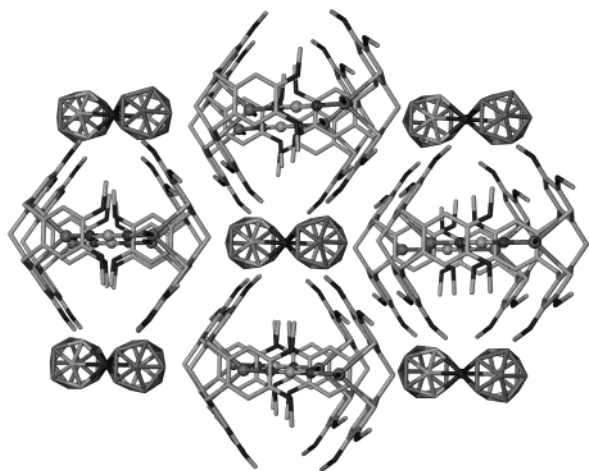
Figure 5. Packing diagram for **2** viewed down the *c* axis. Ag–NCCH₃ atoms shown as spheres.
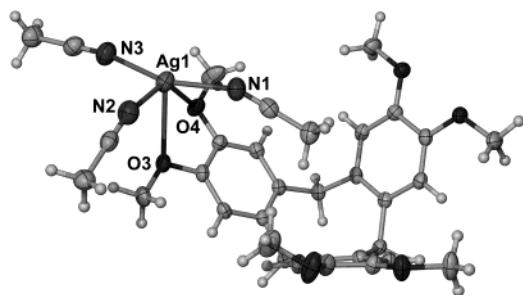

Figure 6. The [Ag(CH₃CN)₃CTV]⁺ cation in **3** illustrating the coordination sphere of Ag⁺ and host–guest interactions between coordinated CH₃CN and CTV. Ellipsoids are shown at 50% probability level.

the structure consists of a [Ag(CH₃CN)₃CTV]⁺ cation, [Co(C₂B₉H₁₁)₂]⁻ anion and a clathrated solvent CH₃CN molecule at 50% occupancy, all on general positions. Selected bond lengths and angles are given in Table 2.

The silver center in **3** has an unusual coordination sphere, comprising three CH₃CN ligands and two methoxy O atoms from the CTV. The Ag–N bond lengths are 2.184(2), 2.206(2), and 2.466(2) Å, and the CH₃CN ligands are arranged in a distorted T-shape; angles are given in Table 2. The Ag(I) coordination sphere is completed by coordination to both O atoms of one of the veratrole moieties within the CTV at long Ag–O distances 2.685(2) and 2.834(2) Å to form a five-membered chelate ring, Figure 6. These distances are consistent with weak coordinate bond formation and are the same as Ag–O distances reported for a weakly chelating nitrate ligand (Ag–O bonds 2.692(11) and 2.895(11) Å).[32] The previously reported example of a Ag–CTV coordination compound has Ag–O distances of 2.694(3) and 2.536(3) Å.[19] The coordination geometry around the Ag(I) may be described as highly distorted trigonal bipyramidal with CH₃CN ligands in the axial positions, and the dimethoxy unit and other CH₃CN comprising the equatorial plane. The closest noncoordinating nearest neighbor to the Ag center is a N atom from a symmetry related [Ag(CH₃CN)₃CTV]⁺ cation. The Ag···N separation of 3.38 Å is too long to indicate significant interaction between the Ag and N. Likewise, the Ag···Ag separation of 4.36 Å does not indicate the presence of any Ag–Ag interactions.[32]
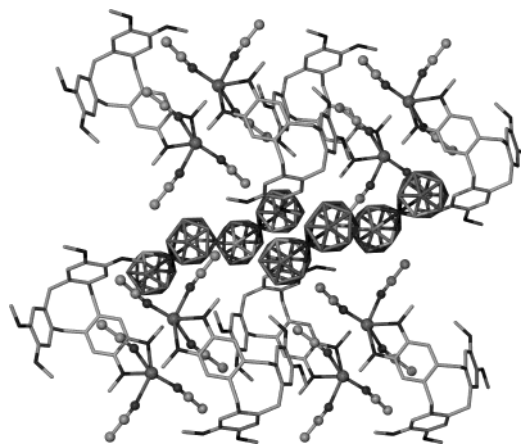

Figure 7. Extended structure of **3**. Hydrogen atoms and solvent CH₃CN are excluded for clarity.

One of the coordinated CH₃CN molecules occupies the CTV molecular cavity to form a host–guest interaction. The guest CH₃CN is parallel to the coordinating veratrole ring of the CTV, Figure 6. The methyl group points toward the center of the CTV as would be anticipated from the hydrophobic effect. The distance between the methyl C and the center of the CTV (−CH₂−)₃ plane is 4.25 Å, which is slightly long when compared with complex **4** and other examples of CTV–aceonitrile host–guest complexes.[17,19]

The extended structure of **3** is a layered structure, Figure 7, with layers of [Ag(CH₃CN)₃CTV]⁺ cations separated by layers of [Co(C₂B₉H₁₁)₂]⁻ anions. The [Ag(CH₃CN)₃CTV]⁺ cations form pairs with the roughly linear CH₃CN–Ag–NCCH₃ links nearly parallel to each other and with the CTV hosts in opposite orientations. The pairs are well separated with the closest contact the Ag···N distance of 3.38 Å. Each [Co(C₂B₉H₁₁)₂]⁻ anion is at hydrogen bonding distances to one CTV arene ring at C−H···π distance 2.78 Å, but do not show other close contacts to other molecular components unlike the in complex **4** described below.

Ag(CH₃CN)₄(CTV)[Co(C₂B₉H₁₁)₂](CH₃CN)₀.₂₅ 4. Complex **4** crystallizes in a triclinic cell and the structure was solved in space group *P*1̄. The unit cell volume is approximately 160 Å³ greater than that of **3**, slightly larger than would be expected purely on the basis of having two extra CH₃CN molecules in the unit cell, assuming a volume of 20 Å³ per non-H atom. The asymmetric unit of the structure consists of molecules of [Ag(CH₃CN)₄]⁺, CTV, and [Co(C₂B₉H₁₁)₂]⁻ on general positions, and a partially occupied CH₃CN disordered across an inversion center. Selected bond lengths and angles are given in Table 2.

The silver center in **4** is bound within a [Ag(CH₃CN)₄]⁺ complex ion that is 4-coordinate with tetrahedral geometry. The Ag–N bond lengths range from 2.226(3) to 2.303(3) Å (Table 2), consistent with previously reported examples of the [Ag(CH₃CN)₄]⁺ cation.[6,33] As was seen with **3**, the Ag-acetonitrile cation is a guest molecule with one coordinated CH₃CN ligand forming a host–guest interaction with the CTV. The guest CH₃CN extends into the CTV molecular cavity and approaches over one of the −CH₂− links of the CTV, in contrast to **3** where the CH₃CN–Ag guest extends over a veratrole face, Figure 8. In **3**, the orientation of the
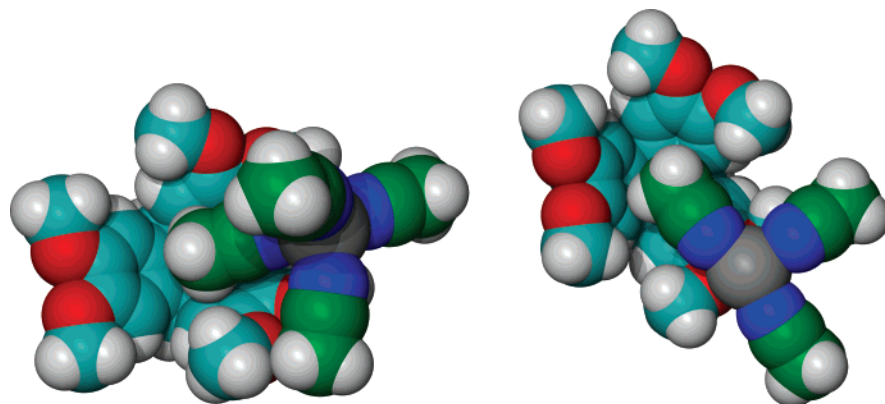
Figure 8. Comparison of host–guest interactions between $[Ag(CH_3CN)_n]^+$ complex ions and CTV in complex **3** (on left) and complex **4** (on right).
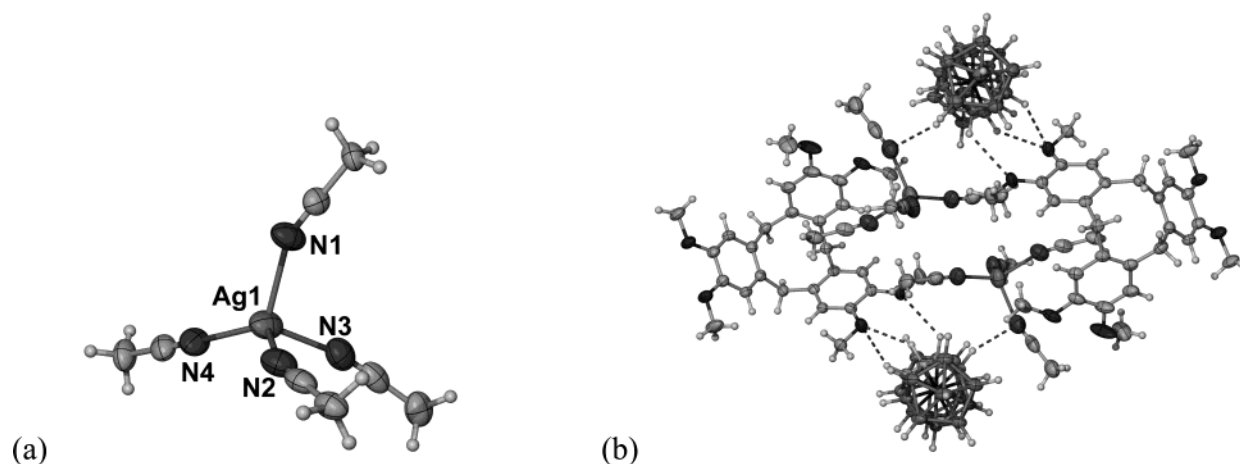

Figure 9. (a) Ag^+ environment in complex **4**; (b) $\{([Ag(CH_3CN)_4] \cap CTV)[Co(C_2B_9H_{11})_2]\}_2$ assembly found in **4**. Close interactions are indicated by dashed lines. Ellipsoids are shown at 50% probability level.

CH_3CN guest is effectively predetermined by the Ag–O coordinate interactions from the CTV methoxy groups; however, this is not the case in **4** and the orientation observed is closer to that found in other examples of intracavity complexation of CH_3CN by CTV.[17,19] The distance between the CH_3CN methyl C and the center of the CTV $(-CH_2-)_3$ plane is 3.99 Å.

Unlike in **3** the $[Co(C_2B_9H_{11})_2]^-$ anion forms close interactions with both the $[Ag(CH_3CN)_4]^+$ cation and CTV molecule. For each molecule of CTV, the methoxy O atoms of a single veratrole moiety are at hydrogen bonding distances to three of the acidic C–H of a $[Co(C_2B_9H_{11})_2]^-$ anion (C–H···O distances 2.52, 2.59, 2.79 Å, corresponding C···O distances 3.48, 3.62, 3.58 Å). These distances are consistent with weak hydrogen bonding.[34] One of the methoxy groups is a birfucated hydrogen bond acceptor. The fourth C–H group of the $[Co(C_2B_9H_{11})_2]^-$ anion is in close contact with a N atom of a coordinated CH_3CN at C–H···N distance 2.51 Å (C···N separation 3.56 Å). This CH_3CN is part of a $[Ag(CH_3CN)_4]^+$ cation that forms host–guest interactions with a CTV molecule adjacent to that which acts as a hydrogen bond acceptor just described, leading to the dimeric $\{([Ag(CH_3CN)_4]^+ \cap CTV)[Co(C_2B_9H_{11})_2]\}_2$ assembly shown in Figure 9. The two $[Ag(CH_3CN)_4]^+$ cations within this dimeric assembly line up such that one of the CH_3CN ligands from each cation are exactly parallel (N(4)–C(24)–C(24)^{IV}–N(4)^{IV} torsion angle 0°, IV = 1 –

x, 1 – y, 1 – z) though in opposite orientations. The distance between the centers of the nitrile groups is 3.92 Å. The silver centers are well separated at Ag···Ag distance 5.65 Å.

The extended structure of **4** is a layered structure with layers of $[Ag(CH_3CN)_4]^+ \cap CTV$ host–guest molecules running along the *bc* diagonal, separated by $[Co(C_2B_9H_{11})_2]^-$ and uncoordinated clathrate acetonitrile molecules. There are no $\pi-\pi$ interactions between the CTV molecules.

Conclusion

The structure of $Ag(CH_3CN)_2[Co(C_2B_9H_{11})_2]$ **1** is a cation–anion coordinate chain with trigonal bipyramidal Ag(I) showing weak B–H···Ag interactions. This is entirely in keeping with the findings of other structural studies of silver carboranes.[6,23–25] Introduction of the host molecule cyclotriveratrylene to $Ag[Co(C_2B_9H_{11})_2]$ in the presence of CH_3CN leads to other possible coordinating ligands and modes for the Ag(I) center, with no B–H···Ag interactions being observed. The number of CH_3CN ligands coordinating to the Ag(I) center has a dramatic effect on the remainder of the Ag(I) coordination sphere. In $Ag(CH_3CN)(H_2O)(CTV)_2[Co(C_2B_9H_{11})_2]$ **2** where there is one CH_3CN ligand, the Ag(I) is 4-coordinate and forms organometallic Ag–C bonds to the CTV host. A higher proportion of CH_3CN

in the crystallization solvent produces $Ag(CH_3CN)_3$-$(CTV)[Co(C_2B_9H_{11})_2](CH_3CN)_{0.5}$ **3**, where the mode of coordination of the CTV to the Ag(I) center has shifted, with the formation of weak coordinate bonds from the methoxy O atoms. When the system is effectively saturated in CH_3CN, the complex $Ag(CH_3CN)_4(CTV)$-$[Co(C_2B_9H_{11})_2](CH_3CN)_{0.25}$ **4** results with a $[Ag(CH_3CN)_4]^+$ cation showing no coordination to the CTV. In all cases, the CTV acts as a host molecule with coordinated acetonitrile as the guest. The complex isolated, and hence Ag(I) coordination mode is dependent on the crystallization conditions.

Supporting Information Available: Crystallographic information files are available free of charge via the Internet at http://pubs.acs.org.

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