

Molecular assembly of 1,3,5-tris(cyano-methyl) and 1,4-bis(cyanomethyl) arenes with silver triflate*

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Abstract: Dicyano- and tricyano-substituted aromatic angular building blocks were systematically complexed with silver triflate, and their structures were determined by means of single-crystal X-ray diffraction. The molecular assembly of 1,3,5-tris(cyanomethyl)-2,4,6-triethylbenzene with silver triflate from benzene resulted in a layered structure with distorted square pyramidal silver sites. The structure resulting from the complexation of 1,3,5-tris(cyanomethyl)-2,4,6-trimethylbenzene with silver triflate is dependent on the solvent of crystallization. From benzene or toluene, reaction of 1,3,5-tris(cyanomethyl)-2,4,6-trimethylbenzene with silver triflate yielded a porous, channel-containing, solvated structure, but from acetone the resulting material was a network solid containing no solvent. Complexation of 1,4-bis(cyanomethyl)-2,3,5,6-tetraethylbenzene and 1,4-bis(cyanomethyl)-2,3,5,6-tetramethylbenzene with silver triflate resulted in network solids where the triflate anions were strongly coordinated to the silver.

Keywords: organonitriles; molecular assembly; silver salts; network solids; X-ray diffraction.

INTRODUCTION

The molecular assembly of multidentate ligands and transition-metal salts for the formation of functional supramolecular species has been of great interest to modern chemists. This is due not only to its theoretical significance for the understanding of the topology of supramolecular networks, but also for its promise for the development of novel materials in such areas as molecular recognition [1], inclusion phenomena [2], and nanoscale molecular devices [3]. However, rational design of the multidentate ligands is essential for the construction of a particular framework with the desired topology, property, and function. Several different approaches, including hydrogen [4] and dative bonding [5], have been used to predetermine molecular assembly. Structures resulting from hydrogen bonding are dependent on the corresponding hydrogen bond donors and acceptors [6]. In another approach, Stang [7] and Fujita [8] have assembled numerous polyhedra using organic polydentate units, which are glued together through the covalent bonding of metal complexes, where the metal is silver, iron, palladium, or platinum. In these cases, there is a variety of angular units which can be combined with either another angular unit

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or a linear unit to form numerous 2D and 3D structures. In yet another approach for the design of nanomaterials, Hoskins and Robson used rigid rod-like organic compounds with different lengths for the formation of nanomolecular structures [9].

By systematically evaluating organic building blocks for their metal-coordinating ability and the structures of the resulting complexes, one might acquire sufficient information to permit the predictable assembly of a variety of desirable supramolecular structures. In our plan, we are interested in using aromatic molecules as angular building blocks with differing metal chelation sites. Our inspiration has been the extensive prior work on the synthesis and conformations of hexaalkylbenzenes. It is well known that the ground-state structure of hexaethylbenzene, as determined both experimentally from its X-ray crystal structure and by computational methods, is one with alternating up-down ethyl groups [10], which is also the dominant conformation in the 1,4-disubstituted-2,3,5,6-tetraethylbenzenes [11–13]. By contrast, in 1,3,5-tris(cyanomethyl)-2,4,6-triethylbenzene, the experimental structure is the perhaps unexpected 5-up/1-down structure [14]. Needless to say, the 1,3,5-trisubstituted-2,4,6-triethylbenzene motif has been utilized in many areas of chemistry [15] from the binding of citrate [16,17] to a synthetic model of enterobactin [18].

Our reasons for choosing polynitrile compounds as our first angular building blocks were two-fold. First, these compounds are easily accessible. 1,3,5-Tris(cyanomethyl)-2,4,6-triethylbenzene [13,14,17], 1,4-bis(cyanomethyl)-2,3,5,6-tetraethylbenzene [13], 1,3,5-tris(cyanomethyl)-2,4,6-trimethylbenzene [19], and bis(cyanomethyl)-2,3,5,6-tetramethylbenzene [20] have been synthesized previously by nucleophilic displacement of the corresponding halides with cyanide; the last is now commercially available. Second, it is known that silver complexes with various organic nitrogen-containing aromatic compounds, such as pyrazines [21] to polynitriles [22,23]. In fact, complexation of silver with organic compounds has led to a wide variety of nanostructures. In 1997, Moore compiled and analyzed coordination complexes from the Cambridge Structural Database using a strict selection process [23]. The structures are classified according to the best fit of the observed structure to an ideal coordination geometry based on the L-M-L bonding angles. At that time, 90 silver-containing structures were divided into eight different geometric classifications. The dominant coordination numbers of silver are 2, 3, and 4. In the first category, both linear and bent geometries have been observed, but linear geometries are most common. Most examples in the tricoordinate category are trigonal planar, but both T-shaped and pyramidal structures are also observed. Finally, tetrahedral, trigonal pyramidal, and square planar structures are observed for the tetracoordinate category, and the tetrahedral geometry is dominant.

In this paper, we report the systematic investigation of the complexation of silver triflate with a number of polynitrile building blocks. The experimental structures of the resulting complexes have been determined by means of single-crystal X-ray analysis, and several aspects of the ligand geometries have been analyzed by using semiempirical [24], *ab initio*, and density functional methods [25]. The nature of these complex structures is dependent on both the ligand and solvent of crystallization.

RESULTS

Crystal structures of ligands

1,3,5-Tris(cyanomethyl)-2,4,6-triethylbenzene (1)

1,3,5-Tris(cyanomethyl)-2,4,6-triethylbenzene was synthesized by chloromethylation of commercially available 1,3,5-triethylbenzene to give the 1,3,5-tris(chloromethyl)-2,4,6-triethylbenzene. Nucleophilic substitution with potassium cyanide produced compound **1** in an overall yield of 68 % [13]. The general information of the complete crystal structure of the ligands and their complexes is given in Table 1. Walsdorff and coworkers have previously determined the structure of **1** by X-ray analysis. Unlike hexaethylbenzene, the arrangement of its substituents in this structure was 5-up/1-down [14]. Our crystallization attempts resulted in crystals with the same structure.

Table 1 Crystal data for compounds/complexes 2–9.

Compound	C ₁₈ H ₂₁ N ₃ · AgCF ₃ SO ₃ (5)	C ₁₅ H ₁₅ N ₃ (2)	C ₁₅ H ₁₅ N ₃ · AgCF ₃ SO ₃ · 1.5C ₆ H ₆ (6)	2C ₁₅ H ₁₅ N ₃ · AgCF ₃ SO ₃ (7)
Formula	C ₁₉ H ₂₁ AgF ₃ N ₃ O ₃ S	C ₁₅ H ₁₅ N ₃	C ₂₅ H ₂₄ AgF ₃ N ₃ O ₃ S	C ₃₁ H ₃₀ AgF ₃ N ₆ O ₃ S
<i>M_r</i>	536.32	237.30	611.40	731.54
Crystal system	Triclinic	Orthorhombic	Monoclinic	Orthorhombic
Space group	<i>P</i> 1	<i>Pnma</i>	<i>P2₁/n</i>	<i>P2₁2₁2₁</i>
<i>a</i> , Å	9.7919 (8)	8.5878 (9)	15.1133 (5)	8.6769 (6)
<i>b</i> , Å	10.4119 (8)	17.1612 (18)	10.6803 (3)	9.0601 (6)
<i>c</i> , Å	11.6410 (9)	9.0709 (9)	17.2704 (6)	39.097 (3)
α, deg.	68.443 (3)	90	90	90
β, deg.	70.157 (2)	90	108.896 (1)	90
γ, deg.	73.657 (4)	90	90	90
<i>V</i> , Å ³	1021.5 (1)	1336.8 (2)	2637.5 (2)	3073.5 (4)
<i>Z</i>	2	4	4	4
ρ (calcd.), g cm ⁻³	1.744	1.179	1.540	1.581
Crystal size	0.27 × 0.25 × 0.06	0.25 × 0.11 × 0.05	0.25 × 0.23 × 0.12	0.20 × 0.19 × 0.08
<i>T</i> , K	200 (2)	200 (2)	200 (2)	200 (2)
<i>F</i> (000)	540	504	1236	1488
μ, mm ⁻¹	1.142	0.072	0.896	0.786
θ _{max}	27.51	22.47	27.46	22.49
Reflections				
Total	8352	4786	14954	10798
Unique	4645	907	6016	4006
Observed	3818	569	3978	3286
<i>R</i> _{int}	0.0280	0.0600	0.0380	0.0569
Parameters	334	167	328	413
<i>R</i> (<i>F</i>) (obs)	0.0298	0.0519	0.0404	0.0407
<i>wR</i> (<i>F</i> ²) (all)	0.0719	0.1419	0.1153	0.0980
<i>S</i> (all)	1.031	1.048	1.021	1.032
Compound	C ₁₈ H ₂₄ N ₂ (3)	C ₁₈ H ₂₄ N ₂ · AgCF ₃ SO ₃ · 1.5C ₇ H ₈ (8)	C ₁₄ H ₁₆ N ₂ (4)	C ₁₄ H ₁₆ N ₂ · AgCF ₃ SO ₃ (9)
Formula	C ₁₈ H ₂₄ N ₂	C _{29.5} H ₃₆ AgF ₃ N ₂ O ₃ S	C ₁₄ H ₁₆ N ₂	C ₁₅ H ₁₆ AgF ₃ N ₂ O ₃ S
<i>M_r</i>	268.39	663.53	212.29	469.23
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>C2/c</i>	<i>C2/m</i>	<i>P2₁/n</i>	<i>P</i> 1
<i>a</i> , Å	9.4419 (5)	16.2952 (6)	8.086 (4)	9.1908 (6)
<i>b</i> , Å	17.1220 (8)	24.0684 (8)	4.375 (2)	9.2776 (7)
<i>c</i> , Å	10.3379 (5)	16.1983 (5)	16.485 (9)	11.2535 (9)
α, deg	90	90	90	101.820 (3)
β, deg	106.989 (2)	99.711 (2)	91.39 (1)	104.168 (3)
γ, deg	90	90	90	106.010 (4)
<i>V</i> , Å ³	1598.3 (1)	6261.9 (4)	583.1 (5)	855.3 (1)
<i>Z</i>	4	8	2	2
ρ (calcd.), g cm ⁻³	1.115	1.408	1.209	1.822
Crystal size	0.25 × 0.10 × 0.06	0.20 × 0.18 × 0.15	0.22 × 0.08 × 0.02	0.20 × 0.10 × 0.03
<i>T</i> , K	200 (2)	200 (2)	200 (2)	200 (2)
<i>F</i> (000)	584	2728	228	468
μ, cm ⁻¹	0.065	0.759	0.072	1.348
θ _{max}	27.51	27.50	22.07	27.40
Reflections				
Total	6110	24147	6186	7173
Unique	1840	7356	722	3847
Observed	1360	3862	455	2664
<i>R</i> _{int}	0.0400	0.0531	0.0910	0.0500
Parameters	139	294	77	230
<i>R</i> (<i>F</i>) (obs) ^a	0.0459	0.0444	0.0557	0.0433
<i>wR</i> (<i>F</i> ²) (all) ^a	0.1247	0.1405	0.1629	0.1062
<i>S</i> (all) ^a	1.037	0.935	1.045	1.017

^a*R*(*F*) = Σ||*F*_o| - |*F*_c||/Σ|*F*_o|; *wR*(*F*²) = [Σ*w*(*F*_o² - *F*_c²)²/Σ*w*(*F*_o²)²]^{1/2}; *S* = goodness-of-fit on *F*² = [Σ*w*(*F*_o² - *F*_c²)²/(*n* - *p*)]^{1/2}, where *n* is the number of reflections and *p* is the number of parameters refined.

1,3,5-Tris(cyanomethyl)-2,4,6-trimethylbenzene (2)

This compound was prepared by the reaction of commercially available 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene with sodium cyanide in *N,N*-dimethylformamide [17]. Crystallization from absolute ethanol gave colorless, orthorhombic needles, space group *Pnma*. In these crystals, the ligand possesses the 3-up conformation (see Fig. 1).

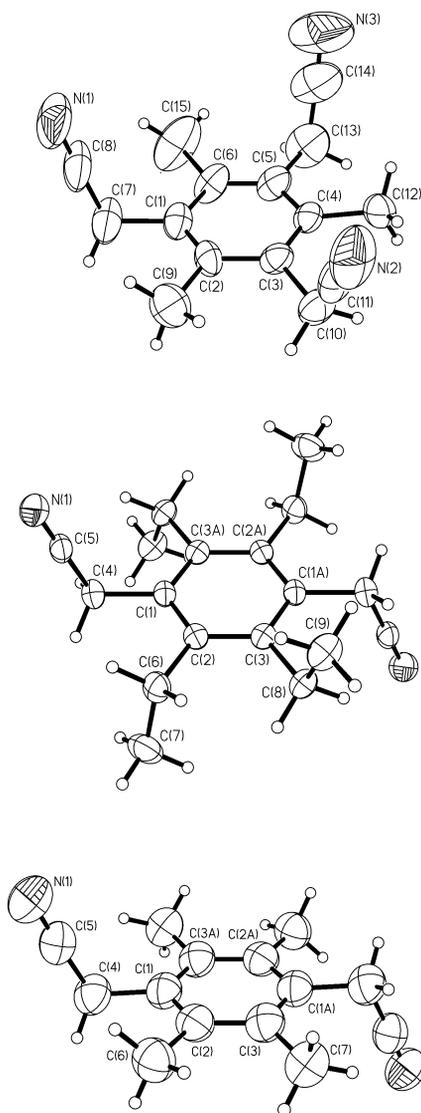


Fig. 1 X-ray structures of 1,3,5-tris(cyanomethyl)-2,4,6-trimethylbenzene (**2**, top), 1,4-bis(cyano-methyl)-2,3,5,6-tetraethylbenzene (**3**, middle), and 1,4-bis(cyanomethyl)-2,3,5,6-tetramethylbenzene (**4**, bottom).

1,4-Bis(cyanomethyl)-2,3,5,6-tetraethylbenzene (3)

1,4-Bis(cyanomethyl)-2,3,5,6-tetraethylbenzene was synthesized by our previously reported four-step procedure from 1,2,4-triethylbenzene [13]. Crystallization of **3** from absolute ethanol produces colorless, monoclinic prisms, space group *C2/c*. In the crystal, this compound exhibits an alternating up-

down configuration as seen in the related molecules, hexaethylbenzene and 1,4-dineohexyl-2,3,5,6-tetraethylbenzene, with similar bond distances and angles.

1,4-Bis(cyanomethyl)-2,3,5,6-tetramethylbenzene (4)

1,4-Bis(cyanomethyl)-2,3,5,6-tetramethylbenzene was synthesized by the reaction of commercially available 1,4-bis(chloromethyl)-2,3,5,6-tetramethylbenzene with cyanide [19]. It gave colorless needles from ethanol, which were monoclinic, space group $P2_1/n$. As with compound **3**, the nitrile functional groups are trans in the crystal structure.

Preparation and structures of the polynitrile complexes of silver triflate

1,3,5-Tris(cyanomethyl)-2,4,6-triethylbenzene silver triflate from benzene (5)

Using a method similar to one previously described [21], a 1:1 mixture of 1,3,5-tris(cyanomethyl)-2,4,6-triethylbenzene and silver triflate was dissolved in toluene and placed in a screw-capped vial. The vial was heated to 125 °C at a rate of 20 °C/h, held at 125 °C for 2 h, and cooled. After seven days, no crystals had formed, so the cap was loosened to enable solvent evaporation. This afforded good-quality crystals suitable for X-ray analysis.

The crystals (triclinic, space group $P\bar{1}$) proved to be a 1:1 silver triflate:compound **1** complex forming a laminar structure consisting of neutral bilayers (Fig. 2). These bilayers are orientated parallel to the crystallographic *ac* plane. The alkyl arrangement (5-up/1-down) observed in the free ligand **1** is retained [14]. All three nitriles coordinate silver ions with an overall trans orientation with respect to the benzene ring. Two of the Ag–N bonds are normal, while the third is noticeably lengthened (Table 2). The bonding of the nitrogens of the ligands provides the “glue” for the monolayers. The bilayers are held together by the triflate (OSO) bridges, which form chair-like, eight-membered rings with each of the arenes facing toward one another. The Ag⋯Ag distance is 4.86 Å. The Ag–O bonds are with one at a normal distance of 2.49 Å, and the second at an elongated distance of 2.64 Å.

Table 2 Selected bond lengths (Å) and angles (deg.) for $C_{18}H_{21}N_3 \cdot AgCF_3SO_3$ (**5**). See Fig. 2.

Ag(1)-N(1)	2.226 (2)	Ag(1)-O(2*)	2.640 (2)
Ag(1)-N(2')	2.246 (2)	Ag(1)-O(1)	2.493 (2)
Ag(1)-N(3'')	2.614 (2)	Ag⋯Ag	4.86
N(1)-Ag(1)-N(2')	153.97 (8)	N(1)-Ag(1)-O(1)	119.41 (7)
N(1)-Ag(1)-N(3'')	97.01 (8)	N(2')-Ag(1)-O(1)	86.60 (7)
N(2')-Ag(1)-N(3'')	83.84 (8)	O(1)-Ag(1)-N(3'')	84.19 (7)
C(8)-N(1)-Ag(1)	162.5 (2)	O(2*)-Ag(1)-N(1)	78.22 (7)
C(12')-N(2')-Ag(1)	148.5 (2)	O(2*)-Ag(1)-N(2')	84.19 (7)
C(16'')-N(3'')-Ag(1)	129.6 (2)	O(2*)-Ag(1)-N(3'')	168.08 (6)

This is not unexpected; triflate is a more strongly coordinating either tetrafluoroborate or hexafluorophosphate [26]. The silver geometry is approximately square pyramidal, with the apical oxygen (O(1), Fig. 2) making angles of approximately 84°, 87°, 108°, and 119° with the silver and the four basal ligands.

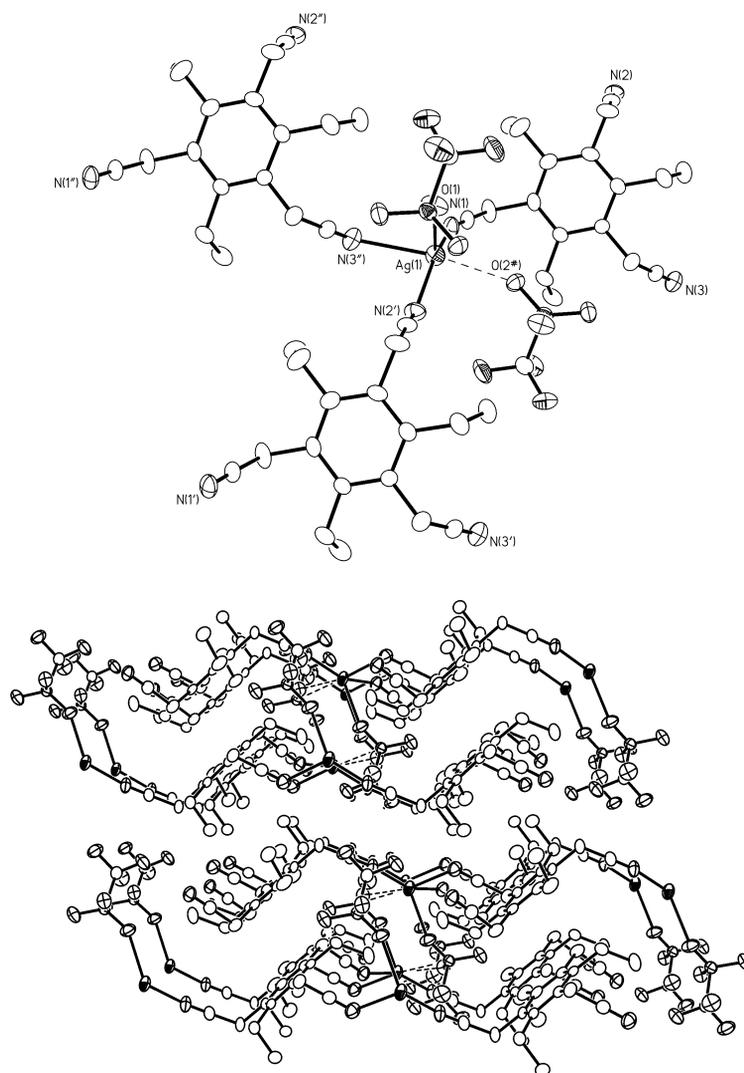


Fig. 2 X-ray crystal structure of complex **5**. The silver coordination environment (top) and the packing of the network solid (bottom) are shown in Fig ?.

1,3,5-Tris(cyanomethyl)-2,4,6-trimethylbenzene silver triflate from benzene (6)

Crystals of complex **6** were prepared as described for complex **5**. The crystals are monoclinic, space group $P2_1/n$, and the resulting solid, like complex **5**, is found to contain a 1:1 silver triflate:ligand composition. Beyond this point, however, the structural similarities between complexes **5** and **6** rapidly diverge. For example, all of the ligand cyano groups are pointed in the same direction in complex **6** (rather than 5-up/1-down as in complex **5**). The silver coordination environment is, nominally, a trigonal planar arrangement of three nitriles, each provided by a different ligand molecule bonding in a cis fashion (Fig. 3).

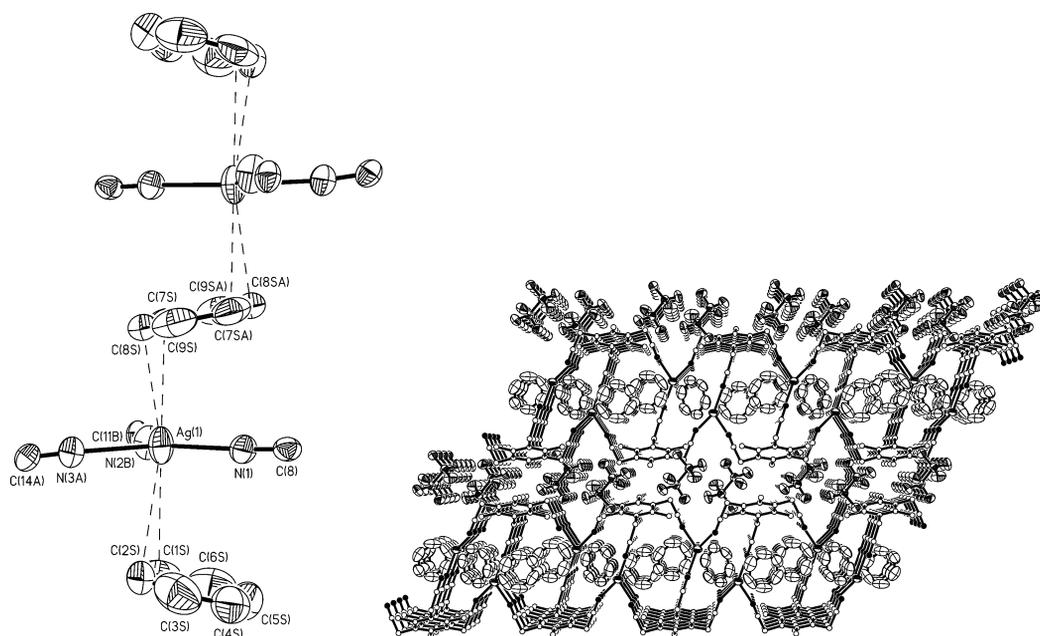


Fig. 3 X-ray crystal structure of complex **6**. The silver coordination environment is shown left, and the packing of the network solid right.

The smallest repeat unit is Ag_4L_4 . The average $\text{Ag}\cdots\text{Ag}$ distance is 6.75 Å. There is no significant lengthening in any of the $\text{Ag}-\text{N}$ bonds, and the average $\text{Ag}-\text{N}$ distance is 2.22 Å (Table 3). Two benzene molecules are also within the van der Waals sphere of each silver ion (Fig. 3). The closest silver-arene contact is 2.98 Å. Similar behavior has been observed in other complexes with $\text{Ag}-\text{C}_{\text{ar}}$ distances as short as 2.45 Å [27]. Consequently, although the silver ions in complexes **5** and **6** are both penta-coordinate, the former exhibits a square pyramidal geometry while the latter is trigonal bipyramidal. Alternating layers of cationic 2D silver-ligand networks and nonbonding triflate anions (ABAB pattern) are observed in the solid state (Fig. 3). Then, benzene solvent molecules are positioned in channels embedded within each cationic layer.

Table 3 Selected bond lengths (Å) and angles (deg.) for $\text{C}_{15}\text{H}_{15}\text{N}_3\cdot\text{AgCF}_3\text{SO}_3\cdot 1.5\text{C}_6\text{H}_6$ (**6**). See Fig. 3.

$\text{Ag}(1)-\text{N}(1)$	2.144 (3)	$\text{Ag}(1)-\text{C}(8\text{S})$	2.977 (3)
$\text{Ag}(1)-\text{N}(2\text{B})$	2.234 (3)	$\text{Ag}(1)-\text{C}(7\text{S})$	3.080 (3)
$\text{Ag}(1)-\text{N}(3\text{A})$	2.280 (3)	$\text{Ag}\cdots\text{Ag}$	6.75
$\text{N}(1)-\text{Ag}(1)-\text{N}(2\text{B})$	119.6 (1)	$\text{C}(8)-\text{N}(1)-\text{Ag}(1)$	177.2 (3)
$\text{N}(1)-\text{Ag}(1)-\text{N}(3\text{A})$	148.7 (1)	$\text{C}(11\text{B})-\text{N}(2\text{B})-\text{Ag}(1)$	168.2 (3)
$\text{N}(2\text{B})-\text{Ag}(1)-\text{N}(3\text{A})$	91.2 (1)	$\text{C}(14\text{A})-\text{N}(3\text{A})-\text{Ag}(1)$	156.1 (3)

Crystallization of **2** with silver triflate from other aromatic solvents, such as nitrobenzene, *o*-, *m*-, and *p*-xylenes, was unsuccessful. This may be due to the greater steric demands of each of these solvents, which would destabilize the cationic polymeric layers. On the other hand, the X-ray crystal structures of compound **2** with silver hexafluorophosphate from benzene and toluene yielded crystals that were isomorphous with those obtained with silver triflate [30].

1,3,5-Tris(cyanomethyl)-2,4,6-trimethylbenzene silver triflate from acetone (7)

Crystallization of compound 2 with silver triflate from acetone yields orthorhombic crystals, space group $P2_12_12_1$. This is quite a different structure than the previous zeolite-like benzene solvate 6. It is another network solid, but it is a 2:1 complex of the ligand and silver salt. The ligands are in the 2-up/1-down conformation, and each ligand uses two of its three cyano nitrogen atoms to coordinate to two silver atoms yielding an infinite 3D network (Fig. 4). The silver coordination is approximately tetrahedral, with four nitrile ligands. These cationic layers alternate with nonbonding triflate anionic layers (Table 4).

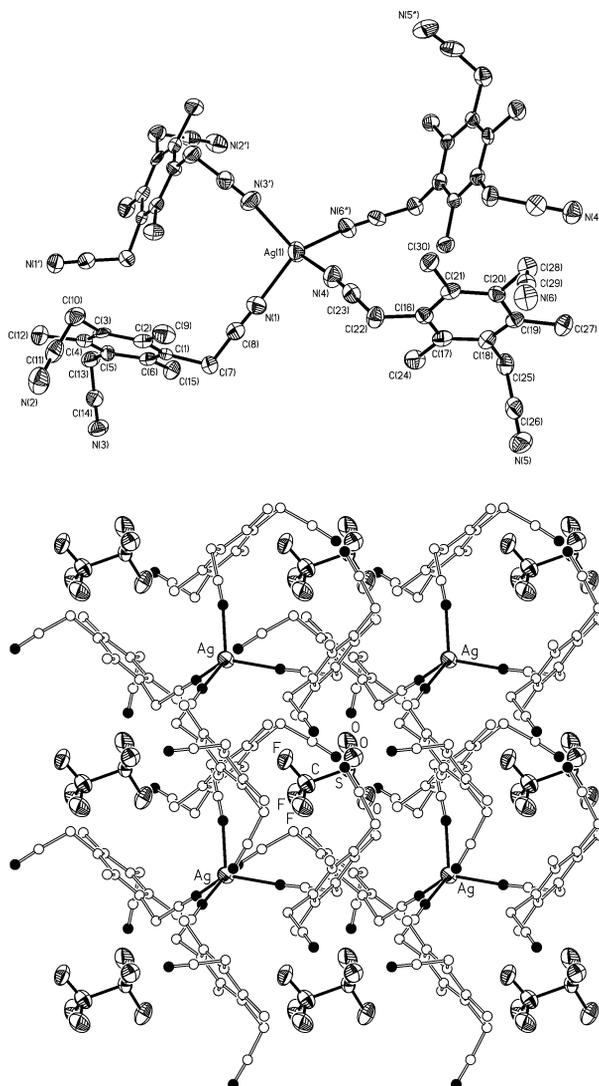


Fig. 4 X-ray crystal structure of complex 7. The silver coordination environment (top) and the packing of the network solid (below) are shown.

Table 4 Selected bond lengths (Å) and angles (deg.) for $2C_{15}H_{15}N_3 \cdot AgCF_3SO_3$ (**7**). See Fig. 4.

Ag(1)-N(6A)	2.255 (5)	Ag(1)-N(3A)	2.277 (6)
Ag(1)-N(1)	2.269 (6)	Ag(1)-N(4)	2.282 (6)
Ag \cdots Ag	11.48		
N(6A)-Ag(1)-N(1)	129.9 (2)	N(3A)-Ag(1)-N(4)	125.5 (2)
N(6A)-Ag(1)-N(3A)	104.7 (2)	C(8)-N(1)-Ag(1)	177.4 (6)
N(1)-Ag(1)-N(3A)	101.3 (2)	C(14A)-N(3A)-Ag(1)	163.1 (5)
N(6A)-Ag(1)-N(4)	99.2 (2)	C(29A)-N(6A)-Ag(1)	162.8 (5)
N(1)-Ag(1)-N(4)	99.4 (2)	C(23)-N(4)-Ag(1)	173.2 (6)

1,4-Bis(cyanomethyl)-2,3,5,6-tetraethylbenzene silver triflate complex from toluene (8)

Crystals were grown from toluene as described for complex **5**, but employing compound **3** as the ligand. The resulting crystals form a network solid in the monoclinic space group $C2/m$ (Fig. 5).

The alternating 3-up/3-down alkyl arrangement of the ligand is retained in this structure, meaning that the nitrile groups are trans with respect to the benzene ring. The silver coordination environment is pseudotetrahedral. The compound exhibits a 2D layered, sheet, or quilted structure. The quilted structure can be described as being constructed from diamond-shaped patches that are roughly 16 Å on a side, i.e., from one Ag(1) \cdots Ag(1) centroid to the nearest neighboring Ag(2) \cdots Ag(2) centroid. The acute and obtuse angles of the diamond are 82.1 and 97.9°, and the Ag(1) \cdots Ag(1) and Ag(2) \cdots Ag(2) distances are 3.93 and 4.05 Å, respectively (Table 5). These neutral 2D nets are further laid one upon the other in the solid state to produce a channel-riddled 3D structure in which the channels are oriented parallel to the crystallographic c axis and filled with disordered toluene solvent molecules.

Table 5 Selected bond lengths (Å) and angles (deg.) for $C_{18}H_{24}N_2 \cdot AgCF_3SO_3 \cdot 1.5C_7H_8$ (**8**). See Fig. 5.

Ag(1)-N(1)	2.184 (3)	Ag(1)-O(1*)	2.426 (6)
Ag(1)-N(2)	2.169 (3)	N(1)-C(8)	1.133 (4)
Ag(1)-O(1)	2.484 (2)	N(2)-C(14)	1.146 (4)
Ag \cdots Ag	3.93, 4.05		
N(1A)-Ag(1)-N(1)	133.8 (1)	N(2)-Ag(2)-O(3)	100.7 (1)
N(1)-Ag(1)-O(1)	101.3 (1)	O(3)-Ag(2)-O(3D)	70.5 (1)
O(1)-Ag(1)-O(1B)	75.4 (1)	C(8)-N(1)-Ag(1)	161.9 (3)
N(2C)-Ag(2)-N(2)	137.3 (1)	Ag(1E)-O(1)-Ag(1)	104.6 (1)

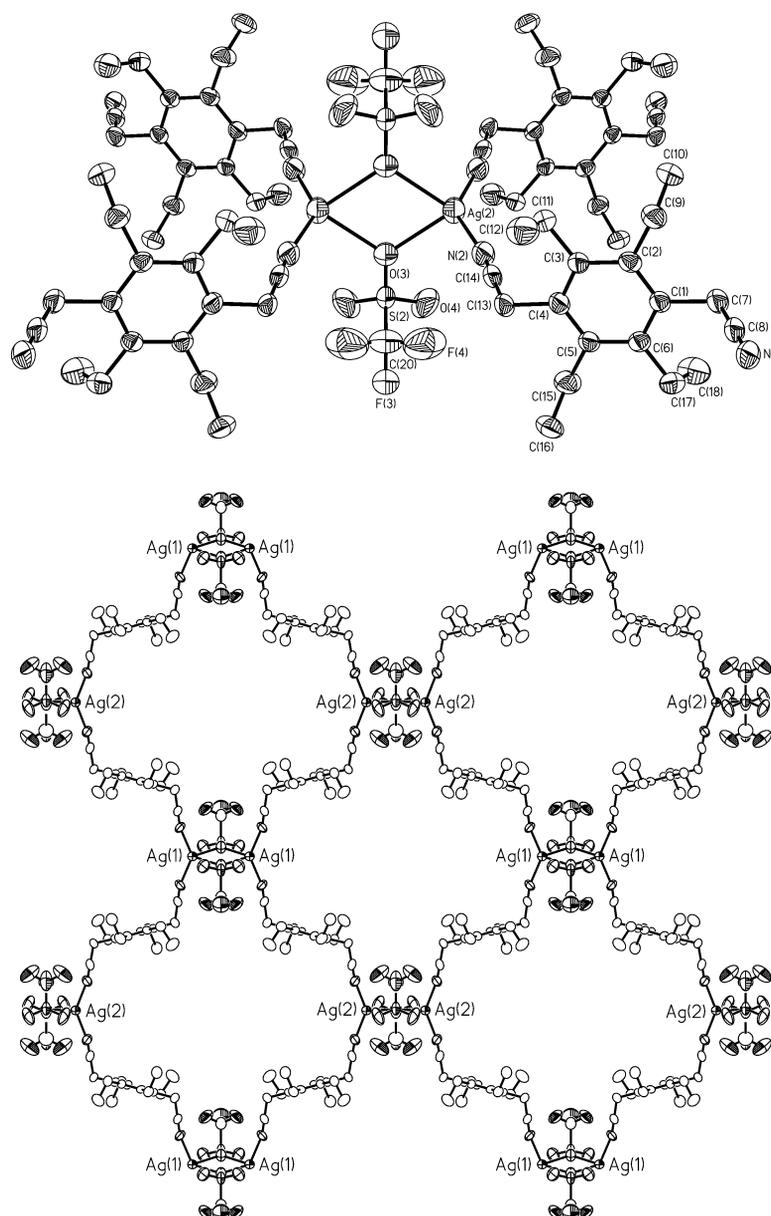


Fig. 5 X-ray crystal structure of complex **8**. The silver coordination environment is shown in the top figure, and the packing of the network solid is shown below.

1,4-Bis(cyanomethyl)-2,3,5,6-tetramethylbenzene silver triflate complex from toluene (9)

Crystallization of **4** with silver triflate from benzene produces yet another layered or sheet-like network solid (Fig. 6). The crystals are triclinic, space group $P\bar{1}$, with a composition ratio that is 1:1 in ligand to silver salt. The ligand's trans cyano groups are retained in the silver complex, and the resulting structure has some similarities to the network solid obtained from 1,3,5-tris(cyanomethyl)-2,4,6-triethylbenzene and silver triflate, e.g., the corrugated ligand layers are held together with bridging oxygens from the triflate anions as in complex **5**.

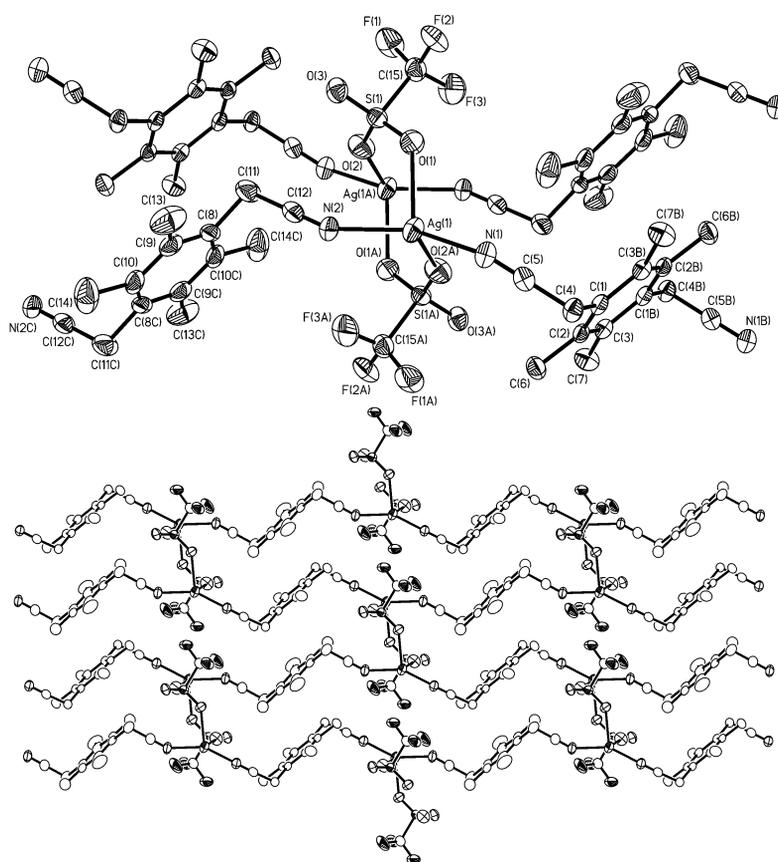


Fig. 6 X-ray crystal structure of complex **9**. The silver coordination environment is shown in the top figure, and the packing of the network solid is shown below.

However, unlike complex **5**, where the silver coordination is approximately square pyramidal, the silver environment in **9** is approximately tetrahedral. This change in geometry and coordination number is accompanied by the expected changes in bond distances, e.g., the average Ag–N and Ag–O distances are shorter in **9** (2.17 and 2.47 Å) relative to those in **5** (2.36 and 2.57 Å) and are listed in Table 6. Somewhat unexpectedly, however, the Ag⋯Ag distances in **9** and **5** show the opposite trend (5.17 vs. 4.86 Å), indicating that these nonbonded distances in such eight-membered Ag₂O₄S₂ motifs are highly subject to steric and packing forces.

Table 6 Selected bond lengths (Å) and angles (deg.) for C₁₄H₁₆N₃·AgCF₃SO₃ (**9**). See Fig. 6.

Ag(1)–N(1)	2.153 (4)	Ag(1)–O(1)	2.446 (3)
Ag(1)–N(2)	2.187 (3)	Ag(1)–O(2A)	2.494 (3)
Ag⋯Ag	5.17		
N(1)–Ag(1)–N(2)	150.5 (1)	O(1)–Ag(1)–O(2A)	97.1 (1)
N(2)–Ag(1)–O(1)	115.8 (1)	C(5)–N(1)–Ag(1)	156.8 (4)
N(1)–Ag(1)–O(2A)	87.5 (1)	C(12)–N(2)–Ag(1)	150.2 (3)
N(2)–Ag(1)–O(2A)	103.7 (1)		

DISCUSSION

In an effort to understand the conformational preferences of 1,3,5-tris(cyanomethyl)-2,4,6-triethylbenzene (**1**) and others that follow, we investigated the structures by a variety of computational methods. Previously, Walsdorff et al. reported, using molecular mechanics, that the 3-up/3-down conformation was 4.4 kcal/mol lower in energy than the observed 5-up/1-down conformation [14]. We examined three different conformations for **1** using semiempirical [24], ab initio, and density functional theory (DFT) methods, and the results are presented in Table 7 [25].

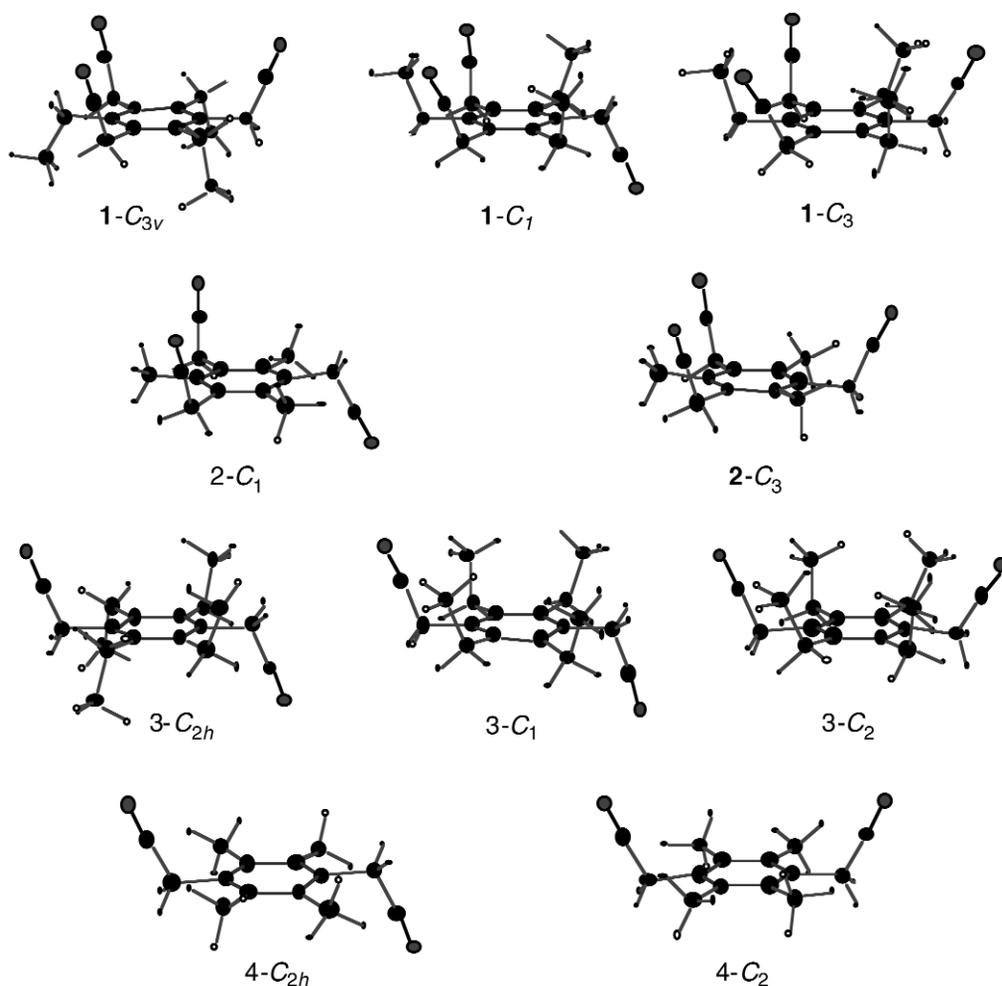
Table 7 Calculated energies of conformations of ligands **1–4**. The relative energies (kcal/mol) of the conformations, normalized to the C_{3v} (3-up/3-down) energy, are in parentheses.

Compound and symmetry	AM1 ^a	HF/3-21G ^a	B3LYP/6-31G(d) ^a
1 C_3 (6-up)	6.2	3.6	2.4
	C_1 (5-up/1-down)	4.3	1.9
	C_{3v} (3-up/3-down)	0.0	0.0
2 C_1 (2-up/1-down)	0.1		
	C_{3v} (3-up)	0.0	
3 C_2 (6-up)	6.7	6.7	4.6
	C_1 (5-up/1-down)	5.0	5.7
	C_{2h} (3-up/3-down)	0.0	0.0
4 C_2 (2-up)	1.1		
	C_{2h} (1-up/1-down)	0.0	

^aEnergy in kcal/mol.

All methods predict that the 3-up/3-down conformation (C_{3v}) is most stable, followed by the 5-up/1-down (C_1) and 6-up (C_3) conformations, but as the computational level increased, the differences in energy between the conformations decreased. Thus, it seems that no one conformation should be strongly favored. In this study, only the 5-up/1-down structure was observed in both the ligand and its triflate complex. The other two conformations are exhibited in the silver hexafluorophosphate salt of **1** from benzene. In light of our previous results for **1**, the two possible conformations of 1,3,5-tris(cyanomethyl)-2,4,6-trimethylbenzene (**2**), the 3-up (C_3) and 2-up/1-down (C_1), were examined only by DFT methods (Table 7). There is no significant preference for either conformation according to these calculations. Although the 3-up conformation is the only one observed in the crystals of the free ligand, it has been shown that its silver triflate complexes exhibit the 2-up/1-down and 3-up structures.

For 1,4-bis(cyanomethyl)-2,3,5,6-tetraethylbenzene (**3**), the alternating 3-up/3-down structure is the calculated and experimentally determined (VT-NMR) [13] lowest energy conformation. Three conformations of **3** were examined computationally: 3-up/3-down (C_{2h}), 5-up/1-down (C_1), and 6-up (C_2). Once again, a decrease in the energy differences among the three conformations is observed with higher-level methods; however, in this case, unlike that of **1**, the energy differences remain substantial. Indeed, in the X-ray structures of both the ligand and its silver triflate complex (vide infra), the most stable 3-up/3-down conformation is observed.



As for 1,4-bis(cyanomethyl)-2,3,5,6-tetramethylbenzene (**4**), the DFT calculations indicate that the observed trans structure is 1.1 kcal/mol more stable than the cis conformation, which is also seen in its triflate complex. Therefore, for the 1,3,5-systems, all of the calculated conformations are observed in the complexes of the solid-state structures. This is probably due to the lower steric congestion of the ethyl groups as well as the directionality of the ligands (meta relative to the benzene face). In the 1,4-systems, the trans orientation is dominant. It is the lowest energy conformation as determined experimentally (solid and solution state) and computationally.

Crystallization of compound **1** from benzene with different silver salts resulted in different solid-state structures that are seemingly counterion-dependent but solvent-independent. This result is not unexpected since triflate is more strongly coordinated than hexafluorophosphate. The silver coordination geometry in complex **5** is square pyramidal having five ligands, two oxygens, and three nitrogens.

In contrast, with 1,3,5-tris(cyanomethyl)-2,4,6-trimethylbenzene as ligand, silver coordination appears to be independent of counterion, but dependent on solvent. Crystallization of **2** with either silver hexafluorophosphate or silver triflate from aromatic solvents results in a solvent-containing channel structure. Crystallization from acetone gives a 3D network solid. Both of these complexes have alternating cationic and nonbonded layers. The former structure is riddled with intralayer channels while the latter structure has no channels. This result is different than that for the 1,3,5-tris(cyanomethyl)-

2,4,6-triethylbenzene, where the triflate anion is strongly associated with the silver, and substitution by hexafluorophosphate gives an entirely different structure [31]. The extra-steric demands of the ethyl groups play a key role in these materials.

When the number of the coordination sites is reduced from three to two as in compounds **3** and **4**, and triflate is the counterion, the resulting complexes are solvent-independent. Both structures contain neutral layers, bridging triflate anions, trans orientation of the nitriles, and a tetrahedral coordination geometry.

CONCLUSION

Several supramolecular structures have been assembled by cocrystallization of bis- and tris(cyanomethyl) arenes and silver triflate. A variety of silver coordination geometries were observed in these materials, and they are summarized in Table 8.

Table 8 Summary of the broad structural features of the organic polynitrile-silver complexes.

Compound	$C_{18}H_{21}N_3 \cdot AgCF_3SO_3$ (5)	$C_{15}H_{15}N_3 \cdot AgCF_3SO_3 \cdot 1.5C_6H_6$ (6)	$2C_{15}H_{15}N_3 \cdot AgCF_3SO_3$ (7)	$C_{18}H_{24}N_2 \cdot AgCF_3SO_3 \cdot 1.5C_7H_8$ (8)	$C_{14}H_{16}N_2 \cdot AgCF_3SO_3$ (9)
Solvent	Benzene	Benzene or toluene	Acetone	Toluene	Toluene
Coordination geometry	Square pyramidal	Trigonal pyramidal	Tetrahedral	Tetrahedral	Tetrahedral
Ag...Ag (Å)	4.86	6.75	11.48	3.93, 4.05	5.17
Solid descript.	Neutral layers (no channels) 2D layered structures	Cationic layers + nonbonded layers (intralayer channels) channel network	Cationic layers + nonbonded layers (no channels), 3D network	Neutral layers (interlayer channels), channel network	Neutral layers (no channels), 2D layered, network
Anion binding	$Ag_2O_4S_2 = 8$ -rings			$Ag_2O_2 = 4$ -rings $Ag_2O_4S_2 = 8$ -rings	$Ag_2O_4S_2 = 8$ -rings
Silver-ligand	Ag_4L_2	Ag_6L_4		Ag_6L_4	Ag_4L_4
Layer type	Double layer	Double layer		Single layer	Single layer
Planarity	Nonplanar	Inplane		Inplane	Inplane
Cis/trans	Trans	Cis	Trans	Trans	Trans

For 1,3,5-tris(cyanomethyl)-2,4,6-triethylbenzene (**1**), only one type of structure was observed upon complexation with silver triflate. With 1,3,5-tris(cyanomethyl)-2,4,6-trimethylbenzene (**2**), the structure of the complex was independent of the counterion used, but dependent on the choice of solvent. Zeolite-like, 1:1 complexes were formed upon crystallization of **2** with silver triflate in aromatic solvents, but crystallization from acetone gave a 2:1 complex containing no solvent. Both complexes of bis(cyanomethyl)benzene derivatives **3** and **4** with silver triflate yielded network solids, but with differing silver coordination environments. With these systems, it is clear that the cyanomethyl groups must be out of plane due to the presence of the methyl or methylene groups, which reduces the number of accessible conformations of the ligand. We are expanding our work to include molecules with rather free rotation as in biscyanomethylbenzenes (*ortho*, *meta*, and *para*) and more fixed structures as in dicyanovinyl arenes with silver and other metal salts to explore the driving forces of molecular assembly.

EXPERIMENTAL SECTION

Melting points are uncorrected. Proton and carbon NMR spectra were recorded at 250 and 62.9 MHz, respectively, on a Bruker AC 250 spectrometer. Unless otherwise stated, commercial reagents were used as supplied. 1,3,5-Tris(cyanomethyl)-2,4,6-triethylbenzene and 1,4-bis(cyanomethyl)-2,3,5,6-tetraethylbenzene were synthesized by literature procedures. Glass vials with Teflon-lined caps were washed with distilled water and oven-dried at 110 °C before use. No special steps were taken to exclude oxygen or moisture during the growth of single crystals.

Preparation of 1,3,5-tris(cyanomethyl)-2,4,6-trimethylbenzene (2): 1,3,5-Tris(bromomethyl)-2,4,6-trimethylbenzene (4.10 g, 10.1 mmol), DMF (100 mL), and sodium cyanide (1.65 g, 33.22 mmol) were added to a 250-mL round-bottom flask, and the mixture was heated at reflux for 2 h, then cooled to room temperature and stirred for 2 days. The reaction was quenched with 300 mL of water, and the resulting white solid was collected by filtration and washed with 100 mL of water. The crude product was collected and dried to give compound **2** (2.16 g, 9.10 mmol, 89 % yield): m.p. 250–252 °C, lit. m.p. 251–253 °C [19a], 256–258 °C [19b]. ¹H NMR (acetone-*d*₆) δ 2.51 (s, 3H), 4.01 (s, 2H); ¹³C{¹H} NMR (CDCl₃) δ 17.1, 19.3, 118.5, 129.5, 136.9.

Preparation of 1,4-bis(cyanomethyl)-2,3,5,6-tetramethylbenzene (4): 1,4-Bis(chloromethyl)-2,3,5,6-tetramethylbenzene [11–13] (2.01 g, 8.7 mmol) was dissolved in acetone (100 mL), and the solution was heated to reflux. Sodium cyanide (1.29 g, 26.9 mmol) was added to the reaction mixture followed by water (30 mL). The reaction mixture was heated at reflux for 12 h. Upon cooling, the solution was poured onto ice (100 mL). The product precipitated as a chalky white powder. The crude product was collected by filtration and dried to give compound **4** (1.32 g, 5.33 mmol, 61 % yield): m.p. 265–266 °C, lit. m.p. 256–258 °C [20a], 269–270 °C [20b]. ¹H NMR (DMSO-*d*₆) δ 3.95 (s, 4H), 3.37 (s, 12H); ¹³C{¹H} NMR (DMSO-*d*₆) δ 16.1, 18.5, 118.7, 128.5, 133.2.

General X-ray crystallographic procedures: X-ray data were collected by using graphite monochromated Mo K α radiation (0.71073 Å) on a Nonius KappaCCD diffractometer. The diffraction data were processed and reduced with DENZO-SMN [28a], PLATON [28b], and Siemens SHELXLT [29]. All structures were solved by direct methods and were refined by full-matrix least-squares on F^2 using SHELXTL. Selected crystal, reflection, and refinement data are summarized in Table 8.

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30. $C_{15}H_{15}N_3 \cdot AgPF_6 \cdot 1.5C_6H_6$, monoclinic, $P2_1/n$, $a = 14.2377$ (4) Å, $b = 10.6924$ (3) Å, $c = 18.0150$ (6) Å, $\beta = 107.797$ (1)°.
31. Crystallization of a 1:1 mixture of compound **1** and silver hexafluorophosphate from benzene or toluene gives cubic crystals (space group $Fd\bar{3}$, $a = 37.3862$ (6) Å (from toluene)) which contain spheroidal complexes of silver and **1** where the silver coordination is trigonal planar, and the conformation of **1** is 6-up (illustrated below). However, although the spheroids are well ordered, and the anions show only moderate disorder, the remainder of the unit cell (nearly 60 % of its volume) is comprised of highly disordered silver complexes of an uncertain structure which have compromised the refinement.

