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Coordination Networks Based on Tetrahedral Silane Building Blocks: Influence of the Anion on Structures Adopted by $Ag^+{-}Si(p\text{-}C_6H_4CN)_4$ Arrays

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The silane tetrakis(4-cyanophenyl)silane (**1**) was prepared by the reaction of 4-lithiobenzonitrile with silicon tetrachloride at −100 °C. This tetrahedral molecular building block crystallizes with AgOTf (OTf = O_3SCF_3) from benzene and dichloromethane to give $[Ag_2Si(p\text{-}C_6H_4CN)_4][OTf]_2{\cdot}2C_6H_6$ (**2**). The extended solid structure of **2** is composed of interpenetrating "double layers" which are 3-connected via trigonal planar Ag and tetrahedral Si centers. The individual nets contain six-membered rings which are folded in one corner along a Si···Si vector to give an envelope conformation. Overall, the structure is heavily cross-linked via −CN−Ag(1)−NC−, −Ag(1)−Ag(2)−NC−, and $-CN-Ag(2)(\mu\text{-}O_3SCF_3)_2Ag(2)-NC-$ linkages. Compound **1** also crystallizes with $AgPF_6$, to give $\{Ag_3[Si(p\text{-}C_6H_4CN)_4]_2\}[PF_6]_3{\cdot}1.6THF{\cdot}0.5C_6H_6{\cdot}CH_2Cl_2$ (**3**). This coordination network also contains 3-connected nets, with six-membered rings in the chair conformation. These nets are interwoven to form the 3-dimensional structure. Compounds **2** and **3** are air-sensitive, and their structures are readily broken up by dissolution in acetone. The network of **2** appears to lose crystallinity when exposed to heat and vacuum (by PXRD) but nonetheless retains some properties as a molecular sieve.

Introduction

Coordination networks based on polyfunctional ligands have attracted considerable attention in recent years, particularly since the pioneering work of Hoskins and Robson.[1] Such systems seem to represent a promising new class of materials which could behave as catalysts and molecular sieves.[1−8] Crystalline lattices built from metal ions and polyfunctional building blocks may possess well-defined pore structures, which could in principle be synthetically modified by the incorporation of catalytic centers. In recent years, relatively rigid coordination networks with sieving properties have been reported.[3c,4a,c,5c] In general, however, such frameworks appear to be relatively unstable toward conditions which might allow them to be used as heterogeneous catalysts or molecular sieves. In part, this is due to the relatively weak coordinate bonds which are used to (self-)assemble and support the lattice. Zeolites, which represent an extremely useful class of porous materials, possess stable frameworks that are reinforced by "double layers" of strong covalent bonds.[9] As originally pointed out by Robson, tetrahedral building blocks offer the potential for large cavities in a coordination network.[1,10] Such centers also offer a relatively high number of connections (4) to the lattice structure, compared to many other building blocks which have been employed involving two or three donor sites.

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Only a few reports have appeared describing coordination networks based on polyfunctional ligands as tetrahedral building blocks. Of course, there are diamond-related frameworks based on metal cyanides such as $Cd(CN)_2$ and $[NMe_4][CuZn(CN)_4]$.[1] A diamond-like structure results from linking the tetrahedral carbon-centered ligand tetrakis(4-cyanophenyl)methane with four-coordinate Cu(I) centers.[1] Large cavities in this structure were occupied by guest solvent and BF_4^- anions. More recently, Lee, Moore, and co-workers have described a structure based on the same tetrahedral building block and 3-connected Ag(I) centers, which consists of undulating 2D nets.[3d] In the latter structure, one nitrile group of each ligand is left uncoordinated.

We reasoned that tetrahedral centers based on silicon might be synthetically accessible and provide readily modified building blocks with a range of structural and chemical properties. Our initial investigations have centered on tetrakis(4-cyanophenyl)silane, which is analogous to the carbon-based building block described previously. Here we report two 3D structures that result from the combination of this building block with Ag(I) centers. It is seen that the nature of the anion and that of the guest solvent play a significant role in defining the framework structure.

Experimental Section

All manipulations were carried out under an atmosphere of nitrogen. Solvents were dried and distilled under nitrogen. Silver reagents were purchased from Aldrich. 4-Bromobenzonitrile was purchased from Fluka. Infrared spectra were obtained with a Perkin-Elmer 1330 spectrometer. Thermal analyses were obtained with a Du Pont model 2000 thermal analysis system. Elemental analyses were determined by the analytical facility in the College of Chemistry at the University of California, Berkeley. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker AM X-300 and VBAMX-400 instruments.

Tetrakis(4-cyanophenyl)silane (1). A solution of *n*-BuLi in hexane (1.6 M, 32.96 mmol, 20.6 mL) was added dropwise to a solution of 4-bromobenzonitrile (6.0 g, 32.96 mmol) in diethyl ether and THF (150 mL, 2:1) at −100 °C. The mixture was stirred for another 1 h after the addition was complete, and then a solution of $SiCl_4$ (8.24 mmol, 0.94 mL) in diethyl ether (10 mL) was added slowly to the resulting suspension at the same temperature. The reaction mixture was warmed to room temperature and stirred for 10 h, and then it was heated for 0.5 h at 40 °C. The volatile material was removed under dynamic vacuum, and the solid was extracted with dichloromethane (120 mL). The resulting solution was concentrated to 50 mL, and hexane (5−10 mL) was added to produce a cloudy solution. The solution was filtered, the filtrate was concentrated to 30 mL, and more hexane (50 mL) was added to precipitate a solid. The solid was recrystallized from ethyl acetate and hexane (50 mL/20 mL) (−32 °C) to give yellow crystals which were heated to 80 °C for 6 h to remove ethyl acetate. The product was isolated as a white solid (2.0 g) in 52% yield. Anal. Calcd for $C_{28}H_{16}N_4Si$: C, 77.06; H, 3.67; N, 12.84. Found: C, 76.81; H, 3.92; N, 12.45. ^1H NMR ($CDCl_3$, 22 °C, 300 MHz): δ 7.76, 7.73, 7.61, 7.58 (AA′BB′ pattern, C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 22 °C, 75.5 MHz): δ 136.8 (CN), 136.5, 131.9, 118.0, 115.0 (C_6H_4). IR (KBr, cm^{-1}): 2229 s sh, 1387 s sh, 1101 s sh, 825 s sh, 596 s sh, 553 s. MS (70 eV, EI): *m/z* 436 (M^+, 68%), 334 ($M^+ - C_6H_4CN$, 100%).

$[Ag_2Si(p\text{-}C_6H_4CN)_4][OTf]_2\cdot 2C_6H_6$ (2). A solution of AgOTf (0.122 g, 0.48 mmol) in 10 mL of benzene was layered over a solution of tetrakis(4-cyanophenyl)silane (0.104 g, 0.24 mmol) in dichloromethane (5 mL). On standing at room temperature for 7 days, the mixture yielded colorless crystals, which appeared on the wall of the tube. The crystals were isolated in a yield of 65% (0.17 g). Anal. Calcd for $C_{42}H_{28}F_6N_4O_6S_2SiAg_2$: C, 45.59; H, 2.53; N, 5.06. Found: C, 45.68; H, 2.75; N, 5.19. IR (KBr, N_2, cm^{-1}): 2355 m, 2329 m, 2254 s, 2231 s, 1288 vs, 1278 vs, 1232 vs, 1024 s, 823 s, 636 s, 599 s.

$\{Ag_3[Si(p\text{-}C_6H_4CN)_4]_2\}[PF_6]_3\cdot 1.6THF\cdot 0.5C_6H_6\cdot CH_2Cl_2$ (3). A solution of **1** (0.087 g, 0.2 mmol) in dichloromethane (5 mL) was layered with 1.0 mL of benzene. Then, a solution of $AgPF_6$ (0.101 g, 0.4 mmol) in THF (5 mL) was carefully layered over the benzene to make a third layer. After 3 days of diffusion at ambient temperature, colorless crystals appeared on the bottom of the Schlenk tube. The crystals (0.102 g, 55%) were collected after 10 days. A sample for elemental analysis was subjected to vacuum for 0.5 h. Anal. Calcd for $C_{66.4}H_{49.8}Cl_2F_{18}N_8O_{1.6}P_3Si_2Ag_3$: C, 42.63; H, 2.68; N, 5.99. Found: C, 43.51; H, 2.88; N, 5.81. IR (KBr, N_2, cm^{-1}): 2364 w, 2335 w, 2254 m, 1388 m, 1101 m, 841 vs, 557 s.

Table 1. Crystallographic Data for Compounds **2** and **3**

	2	**3**
	(a) Crystal Parameters	
empirical formula	$C_{42}H_{28}F_6N_4O_6S_2$-$SiAg_2$	$C_{34.5}H_{26}Cl_2ON_4F_9P_{1.5}$-$SiAg_{1.5}$
fw	1106.64	990.85
cryst color, habit	colorless, prism	colorless, tabular
cryst size, mm	0.10 × 0.20 × 0.27	0.08 × 0.17 × 0.27
crystal system	monoclinic	triclinic
space group	$C2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	14.0393(9)	10.9982(1)
b, Å	22.701(1)	13.8573(2)
c, Å	14.4981(9)	15.1457(3)
α, Å		107.174(1)
β, deg	108.300(1)	108.296(1)
γ, deg		102.426(1)
V, Å^3	4386.9(4)	1969.59(7)
Z	4	2
ρ(calc), g cm^{-3}	1.675	1.671
μ(Mo Kα), cm^{-1}	10.89	10.55
temp, °C	−90	−125
	(b) Data Collection	
diffractometer	Siemens SMART	Siemens SMART
radiation (λ, Å)	Mo Kα (0.710 69)	Mo Kα (0.710 69)
	(c) Refinement	
rfln:param ratio	8.95	7.88
$R(F)$, %	4	6.3
$R_w(F)$, %	4.9	7.4

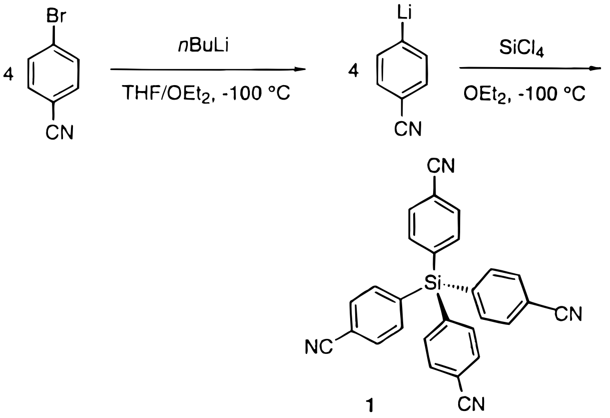
Benzene/Benzene-d_6 Exchange in 2. A sample of **2** (0.050 g) was soaked in 1 mL of benzene-d_6 for 3 h. The benzene-d_6 was removed by filtration, and then the sample was dried briefly under vacuum. By ^1H NMR spectroscopy, the sample contained 0.21 mol of benzene/mol of **1**. The TGA analysis of this sample revealed a weight loss of 10.7%, which corresponds to 1.24 mol of benzene-d_6 and 0.21 mol of benzene/mol of **1**.

Crystallographic Structure Determinations. Crystallographic data for **2** and **3** are collected in Table 1. A colorless prism of **2** with dimensions 0.10 × 0.20 × 0.27 mm was mounted on a glass fiber using Paratone N hydrocarbon oil. The mounted crystal was placed under a cold stream of nitrogen (−90 °C) on the diffractometer. Data were collected using a Siemens SMART diffractometer with a CCD area detector. A preliminary orientation matrix and unit cell parameters were determined by collecting 60 10-s frames, followed by spot integration and least-squares refinement. A volume including one unique quadrant of data was collected using ω scans of 0.3° and a collection time of 10 s per frame. Frame data were integrated (*XY* spot spread = 1.6°; *Z* spot spread = 0.6°) using SAINT. The data were corrected for Lorentz and polarization effects. An absorption correction was performed using XPREP ($\mu R = 0.05$, $T_{max} = 0.92$, $T_{min} = 0.83$). The 20 124 integrated reflections were averaged to give 7973 unique reflections ($R_{int} = 0.035$). Of these, 5300 reflections were considered observed ($I > 3.00\sigma(I)$). No decay correction was necessary. The structure was solved using direct methods (SIR92), expanded using Fourier techniques (DIRDIF92), and refined by full-matrix least-squares methods using teXsan software. One of the two triflate anions is mildly disordered in its location and was modeled with 78% and 22% populations, respectively. The non-hydrogen atoms, except the partially occupied atoms in the disordered triflate anions, were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms in the silane ligand were included in calculated positions but not refined. Hydrogen atoms in one benzene ring were included as located on a difference Fourier map. The number of variable parameters was 592 giving a data:parameter ratio of 8.95. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.90 and -0.64 e/Å^3, respectively.

A colorless tabular crystal of **3** with dimensions 0.08 × 0.17 × 0.27 mm was mounted on a glass fiber using Paratone N hydrocarbon oil. The mounted crystal was placed under a cold stream of nitrogen (-125 °C) on the diffractometer. Data was collected using a Siemens SMART diffractometer with a CCD area detector. A preliminary orientation matrix and unit cell parameters were determined by collecting 60 10-s frames, followed by spot integration and least-squares refinement. A volume including one unique quadrant of data was collected using ω scans of 0.3° and a collection time of 20 s per frame. Frame data was integrated (XY spot spread = 1.6°; Z spot spread = 0.6°) using SAINT. The data were corrected for Lorentz and polarization effects. An absorption correction was performed using XPREP ($\mu R = 0.12$, $T_{\max} = 0.95$, $T_{\min} = 0.75$). The 8301 integrated reflections were averaged to give 5528 unique reflections ($R_{\text{int}} = 0.026$). Of these, 4073 reflections were considered observed ($I > 3.00\sigma(I)$). No decay correction was necessary. The structure was solved using direct methods (SIR92), expanded using Fourier techniques (DIRDIF92), and refined by full-matrix least-squares methods using teXsan software. The structure refined with the approximate formula $C_{34.5}H_{26}Cl_2F_9ON_4P_{1.5}SiAg_{1.5}$. All fully-occupied non-hydrogen atoms were refined anisotropically, as were the majority components of the disordered atoms. All other non-hydrogen atoms were refined isotropically. Hydrogen atoms in the silane ligand were included in calculated positions but not refined. The number of variable parameters was 517, giving a data:parameter ratio of 7.88. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.77 and -0.78 e/Å^3, respectively.

Results

Synthesis of Tetrakis(4-cyanophenyl)silane (1). 4-Bromobenzonitrile was lithiated using *n*-BuLi in hexane at low temperature (-100 °C), and the resulting lithium derivative was reacted with 0.25 equiv of silicon tetrachloride in ether/THF to produce **1** as a white solid (eq 1). To obtain product, the reaction mixture must be kept at -100 °C during the additions of *n*-BuLi and SiCl$_4$.[11] Pure **1** was obtained in about 52% yield after crystallization from ethyl acetate/hexane (2:1) and drying under vacuum at 80 °C. This compound is soluble in tetrahydrofuran, toluene, and dichloromethane but not in saturated hydrocarbons. It crystallizes from ethyl acetate with incorporation of 0.5−0.8 equiv of solvent.



(1)

The thermal stability of **1** was examined by TGA (thermal gravimetric analysis). The TGA trace for **1** reveals an onset temperature for decomposition at 319 °C, and a rather dramatic weight loss continues thereafter until about 504 °C. A more gradual weight loss of 5% then occurs to 1000 °C.

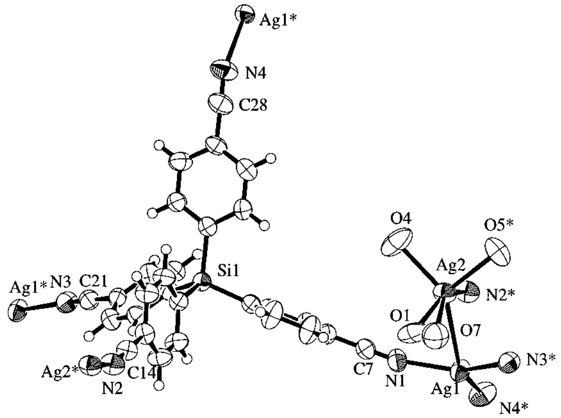


Figure 1. ORTEP drawing of the local environment about the tetrahedral center in **2**.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for [Ag$_2$Si(*p*-C$_6$H$_4$CN)$_4$][OTf]$_2$•2C$_6$H$_6$ (**2**)

(a) Bond Distances			
Ag(1)−Ag(2)	3.1100(6)	Ag(1)−N(1)	2.208(5)
Ag(1)−N3	2.197(5)	Ag(1)−N(4)	2.334(5)
Ag(2)−N(2)	2.257(4)	Ag(2)−O(1)	2.241(5)
Ag(2)−O(4)	2.390(4)	Ag(2)−O(5)	2.402(4)
Ag(2)−O(7)	2.35(3)	Si(1)−C(1)	1.871(5)
Si(1)−C(8)	1.87(5)	Si(1)−C(15)	1.885(5)
Si(1)−C(22)	1.885(5)	S(2)−O(4)	1.423(4)
S(2)−O(5)	1.439(4)	S(2)−O(6)	1.424(4)
(b) Bond Angles			
N(1)−Ag(1)−N(3)	146.4(2)	N(1)−Ag(1)−N(4)	102.0(2)
N(3)−Ag(1)−N(4)	111.2(2)	Ag(2)−Ag(1)−N(1)	78.1(1)
Ag(2)−Ag(1)−N(3)	72.7(1)	Ag(2)−Ag(1)−N(4)	141.4(1)
Ag(1)−Ag(2)−O(1)	82.4(2)	Ag(1)−Ag(2)−O(4)	134.2(2)
Ag(1)−Ag(2)−O(5)	122.2(1)	Ag(1)−Ag(2)−O(7)	82.3(7)
Ag(1)−Ag(2)−N(2)	59.9(1)	O(1)−Ag(2)−O(4)	99.2(2)
O(1)−Ag(2)−O(5)	120.4(3)	O(1)−Ag(2)−O(7)	21.1(6)
O(1)−Ag(2)−N(2)	140.0(2)	O(4)−Ag(2)−O(5)	96.6(2)
O(4)−Ag(2)−N(2)	98.4(2)	O(5)−Ag(2)−N(2)	92.7(2)
C(1)−Si(1)−C(8)	108.5(2)	C(1)−Si(1)−C(15)	112.5(2)
C(1)−Si(1)−C(22)	108.6(2)	Ag(1)−N(1)−C(7)	163.5(4)
Ag(1)−N(3)−C(21)	171.3(5)	Ag(1)−N(4)−C(28)	151.2(5)
Ag(2)−N(2)−C(14)	155.0(4)	O(4)−S(2)−O(5)	114.1(3)
O(4)−S(2)−O(6)	114.1(3)	O(5)−S(2)−O(6)	116.7(3)

[Ag$_2$Si(*p*-C$_6$H$_4$CN)$_4$][OTf]$_2$•2C$_6$H$_6$ (2). Crystals of this material were obtained by a slow diffusion method. A benzene solution of silver triflate was layered above a dichloromethane solution of **1**, and after 7 days, crystals had formed near the original solvent interface. Complex **2** crystallized as colorless prisms in space group $P2_1/n$ with four crystallographically equivalent [Ag$_2$Si(*p*-C$_6$H$_4$CN)$_4$][OTf]$_2$•2C$_6$H$_6$ asymmetric units per unit cell. Selected geometric parameters for the structure are listed in Table 2. Each nitrile group in the structure is coordinated to silver (Figure 1). The Ag(1) atoms bridge three Si(*p*-C$_6$H$_4$CN)$_4$ ligands and possess a weak interaction (3.1100(6) Å) with Ag(2).[12] The latter Ag(2) centers are bonded to the nitrile group of a Si(*p*-C$_6$H$_4$CN)$_4$ molecule, the oxygen atom of a terminal triflate group (disordered between sites O(1) and O(7)), and two oxygen atoms (O(4) and O(5)) of triflate groups that bridge to another Ag(2) center.[13] The Ag(2)(μ-O$_3$SCF$_3$)$_2$-Ag(2) groups, which form eight-membered rings (Figure 2), possess an inversion center at $^1/_2$, $^1/_2$, 0. Thus, the Si(*p*-C$_6$H$_4$-

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[11] A similar observation was made for the synthesis of R$_n$P(C$_6$H$_4$CN)$_{3-n}$ (n = 1, 2, 3) derivatives: Ravindar, V.; Hemling, H.; Schumann, H.; Blum, J. *Synth. Commun.* **1992**, *22*, 841.

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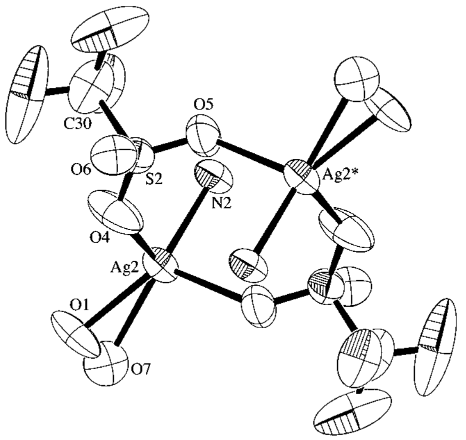

Figure 2. View of the $Ag_2O_4S_2$ rings in the structure of **2**. Only the silver-bound oxygen atoms of the terminal triflate groups are shown (disordered over two positions).

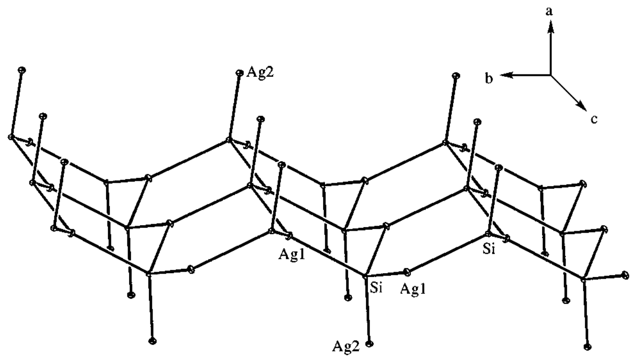

Figure 3. A single 3-connected layer in **2**. Only the Si, Ag(1), and Ag(2) atoms are shown. Therefore, the "bonds" represent $-C_6H_4CN-$ groups.

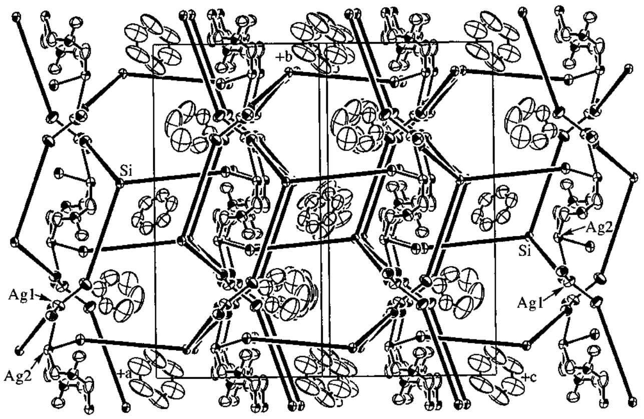

Figure 4. View down the interpenetrating layers of **2**, showing the CN−Ag(2)−Ag(1) linkages. The terminal triflate groups are omitted for clarity.

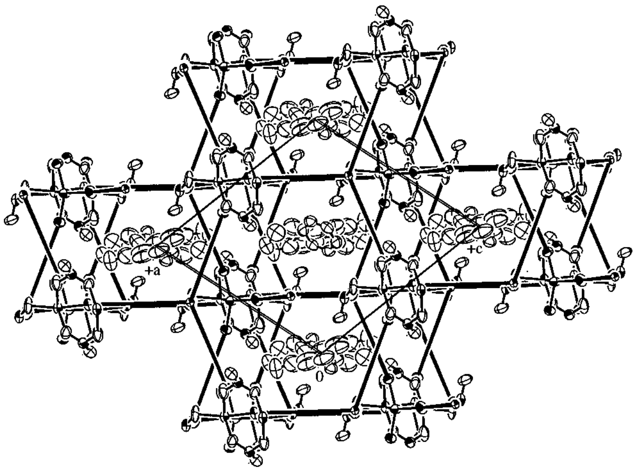

Figure 5. An alternative view of **2**, illustrating the cross-linked nature of the structure and the position of the benzene solvent in the structure.

CN)$_4$ groups in this structure are connected by −CN−Ag(1)−NC−, −CN−Ag(1)−Ag(2)−NC−, and −CN−Ag(2)(μ-O_3SCF_3)$_2$Ag(2)−NC− linkages.

The structure consists of interpenetrated "double layers",[14] which are composed of two nets of six-membered rings folded in one corner along an Si···Si vector to give an "envelope" conformation. These nets are 3-connected via trigonal planar Ag(1) and tetrahedral Si centers, which are linked by $-C_6H_4$-CN "rods" (Figure 3). The $-C_6H_4CN$ arms which protrude above and below each layer coordinate to Ag(2) centers, which serve as linkages (via the −Ag(1)−Ag(2)−NC− connections) to another double layer. Thus, the structure is heavily cross-linked in nature (Figures 4 and 5). The benzene molecules occupy small voids in the structure (between the double layers), but no large pores are present (Figure 5). The benzene molecules are arranged in a zigzag fashion along the *b* axis, but they appear to be isolated and tightly bound in the structure, which does not possess free channels.

The infrared spectrum of **2** exhibits bands for the nitrile groups (at 2355, 2329, 2254, and 2231 cm^{-1}) which are blue-shifted relative to the band for the nitrile groups of **1** (at 2229 cm^{-1}).[15] Compound **2** is highly air-sensitive, and upon exposure of a KBr pellet of the compound to air for 2 h, the infrared ν(CN) stretches disappear and are replaced by bands attributed to **1**. Complex **2** dissolves in acetone, and a spectrum in acetone-d_6 confirmed the 2:1 ratio of benzene to **1** that was observed by X-ray crystallography. Therefore NMR spectroscopy represents a convenient tool to analyze samples of **2** for their content of guest molecules. Immediately after isolation and brief (1 min) exposure to vacuum, the benzene content is ca. 1.8 equiv.

Thermogravimetric analysis of **2** revealed a clean weight loss of 14% before 185 °C, which corresponds to two benzene molecules per formula unit of **1**. Under a dynamic vacuum at room temperature, bulk samples of **2** lose ca. 1 equiv of benzene over 1.5 h. All of the benzene was removed by heating to 190 °C for 1 h under vacuum, and benzene was slowly lost from solid samples of **2** stored under nitrogen. This solvent loss is accompanied by destruction of the crystalline lattice (by PXRD).

The sieving properties of **2** were briefly examined. Exposure of a freshly prepared sample of **2** (containing 1.8 mol of benzene/mol of **1**) to excess benzene-d_6 for 3 h produced a sample that contained 0.21 mol of benzene (by ^{1}H NMR spectroscopy), and analysis by TGA indicated that the sample also contained 1.24 mol of benzene-d_6.

Despite the loss of crystallinity for **2** upon removal of its guest molecules (under vacuum at 190 °C), it retains some properties as a molecular sieve. Analysis of this material by ^{1}H NMR spectroscopy showed that all the benzene had been removed. The BET surface area (nitrogen absorption) of the sample was measured to be only 0.1 m^2 g^{-1}. This sample was then immersed in benzene for 24 h, isolated, and then briefly exposed to vacuum to remove free benzene. Analysis of the material by ^{1}H NMR spectroscopy and TGA revealed the

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(14) A similar structural feature was observed in AgC(CN)$_3$: Vranka, R. G.; Amma, E. L. *Inorg. Chem.* **1966**, *5*, 1020.

(15) (a) Ohba, M.; Okawa, H.; Fukita, N.; Hashimoto, Y. *J. Am. Chem. Soc.* **1997**, *119*. 1011. (b) Ohba, M.; Maruono, N.; Okawa, H.; Enoki, T.; Latour, J.-M. *J. Am. Chem. Soc.* **1994**, *116*, 11566. (c) Storhoff, B. N.; Lewis, H. C., Jr. *Coord. Chem. Rev.* **1977**, *23*, 1.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for $\{Ag_3[Si(p\text{-}C_6H_4CN)_4]_2\}[PF_6]_3\cdot1.6THF\cdot0.5C_6H_6\cdot2CH_2Cl_2$ (**3**)

(a) Bond Distances			
Ag(1)−O(1)	2.29(1)	Ag(1)−N(1)	2.249(7)
Ag(1)−N(2)	2.221(7)	Ag(1)N(3)	2.256(7)
Ag(2)−Ag(3)	1.34(2)	Ag(2)−N(4)	2.057(9)
Ag(3)−N(4)*	2.42(2)	Ag(3)−N(4)	2.50(2)
Si(1)−C(1)	1.875(7)	Si(1)−C(8)	1.867(7)
Si(1)−C(15)	1.890(7)	Si(1)−C(22)	1.866(8)
(b) Bond Angles			
O(1)−Ag(1)−N(1)	107.2(3)	O(1)−Ag(1)−N(2)	116.0(4)
O(1)−Ag(1)−N(3)	92.7(4)	N(1)−Ag(1)−N(2)	115.4(3)
N(1)−Ag(1)−N(3)	108.8(3)	N(2)−Ag(1)−N(3)	114.3(2)
N(4)−Ag(2)−N(4)*	180.0	N(4)−Ag(3)−N(4)*	113.7(7)
C(1)−Si(1)−C(8)	109.1(3)	C(1)−Si(1)−C(15)	108.1(3)
C(1)−Si(1)−C(22)	114.0(3)	C(8)−Si(1)−C(15)	109.9(3)
C(8)−Si(1)−C22)	109.1(3)	C(15)−Si(1)−C(22)	106.5(3)
Ag(1)−N(1)−C(7)	171.4(7)	Ag(1)−N(2)−C(14)	178.9(7)
Ag(1)−N(3)−C(21)	177.1(7)	Ag(2)−N(4)−C(28)	163.0(8)
Ag(3)−N(4)−C(28)	129.2(8)	Ag(3)*−N(4)−C(28)	164.5(9)

presence of 1.1 equiv of benzene (per **1**). The selectivity of this solvent incorporation was tested by exposing a sample of **2** which had been exhaustively dried to a 1:1 mixture of benzene and toluene. The ^{1}H NMR spectrum of the sample revealed the incorporation of 0.71 mol of benzene and 0.63 mol of toluene/mol of **1**. A TGA trace for the latter sample indicated the loss of benzene (11.2% by weight), which is consistent with results from the NMR analysis.

$\{Ag_3[Si(p\text{-}C_6H_4CN)_4]_2\}[PF_6]_3\cdot1.6THF\cdot0.5C_6H_6\cdot CH_2Cl_2$ (3). This material was prepared by a method similar to that used for **2**, except that the layering pattern involved a solution of **1** in dichloromethane, pure benzene, and then a THF solution of $AgPF_6$. The intermediate benzene layer was required for the formation of X-ray-quality crystals, which appeared over the course of about 10 days. The infrared spectrum of **3**, like that of complex **2**, contains infrared stretching bands for the nitrile groups (2364, 2335, and 2254 cm^{-1}) which are blue-shifted relative to those for **1**. Samples of this network solid dissolve in acetone-d_6 to give a solution of **1**, $AgPF_6$, and liberated solvent. Thus the stoichiometry of **3** was established by ^{1}H NMR spectroscopy, and this result is approximately consistent with the elemental analysis. After isolation from the crystallization solvent, crystals of **3** slowly desolvate. This desolvation apparently accounts for the slight difference in the formulas determined by ^{1}H NMR spectroscopy and X-ray crystallography.

Crystals of **3** were transferred directly from solution to Paratone N oil, which provided an inert, hermetic seal. The structure was determined by X-ray crystallography; important bond distances and angles are listed in Table 3. The structure possesses a 2:3 ratio of **1** to Ag$^+$, and an ORTEP view of the local environment about the tetrahedral centers is given in Figure 6.

Crystals of **3** contain two types of Ag positions. The Ag(1) atoms are coordinated to three nitrile groups and link molecules of **1** into a 3-connected net composed of six-membered rings in the chair conformation. These silver atoms have a coordination site filled by either benzene or THF, which refined as intertwined and disordered molecules (Figure 7). Occupancy factors for atoms in the disordered solvent molecules refined to values ranging from 0.30 to 1.00 for benzene and from 0.31 to 1.00 for THF, and it proved difficult to establish a reasonable benzene:THF ratio from the crystallographic data alone. Furthermore, the Ag(1)−C(benzene) distances range from 2.90 to 3.91 Å and represent distances that are somewhat outside the range expected for a Ag−C_6H_6 bonding interaction (2.4−2.5 Å).[16] However, the disorder of the solvent is expected to lead to large errors associated with these distances.

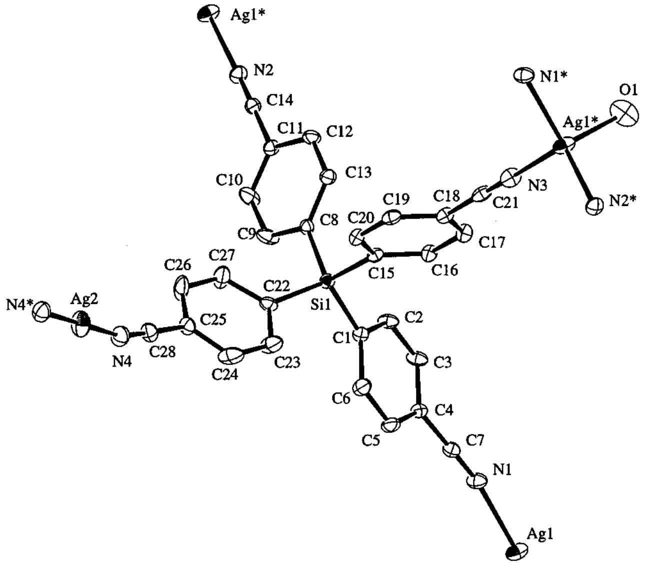

Figure 6. ORTEP drawing of the local environment about the tetrahedral centers in **3**.

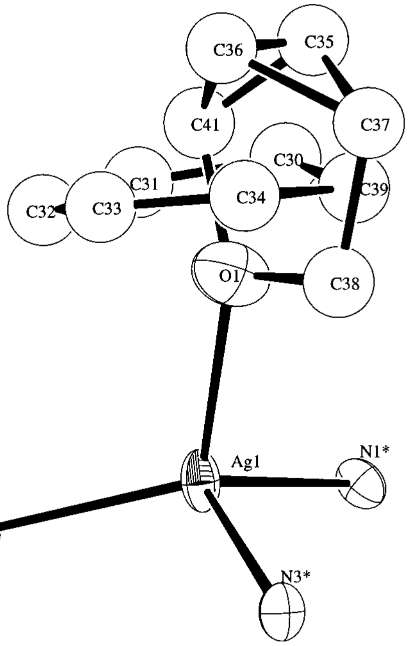

Figure 7. View of the coordination environment about the Ag(1) centers of **3**.

The remaining nitrile groups of the tetrahedral centers protrude from the Ag(1)−**1** 3-connected layers and point in the same direction, roughly perpendicular to the plane of the 3-connected net. An inverted net of the same type is interwoven with the first so that nitrile groups extend from both sides of a "double layer" (Figure 8). These interwoven double layers are connected via coordination of their "dangling" nitrile groups by two-coordinate Ag(2) centers to form an extended lattice (Figure 9). Two lattices of this type interpenetrate to give the entire structure. Cavities in the structure are occupied by the PF_6^- anions and dichloromethane.

An alternative description of the structure is based on repeating double layers of the type shown in Figure 10. These double layers are based on two nets of tetrahedral Si and Ag(1) centers which are linked in a "face-to-face" manner via the Ag(2) connections and are truncated on either side by Ag(1)−

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[16] Shelly, K.; Finster, D. C.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1985**, *107*, 5955.

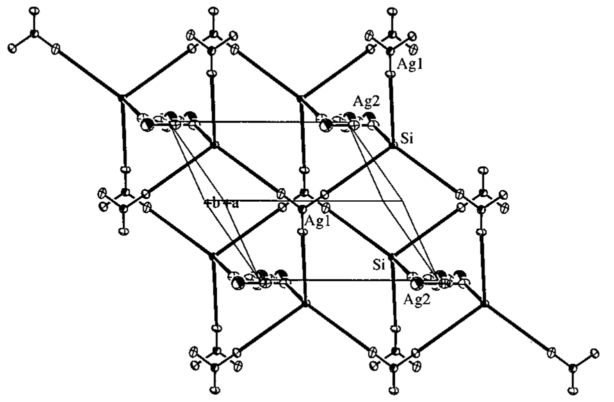

Figure 8. View of a portion of a double layer in **3**, along the perpendicular direction. The PF_6^- ion, the Ag(3) atom, and solvent molecules are omitted for clarity.

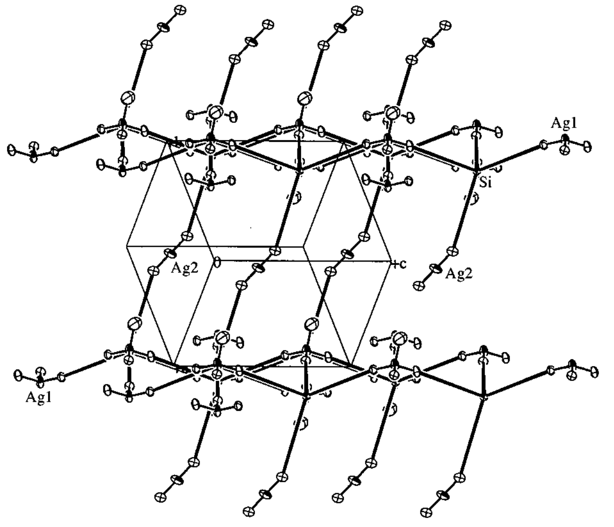

Figure 9. Two double layers of **3** linked together via the Ag(2) atoms. The Ag(3) atoms are omitted for clarity.

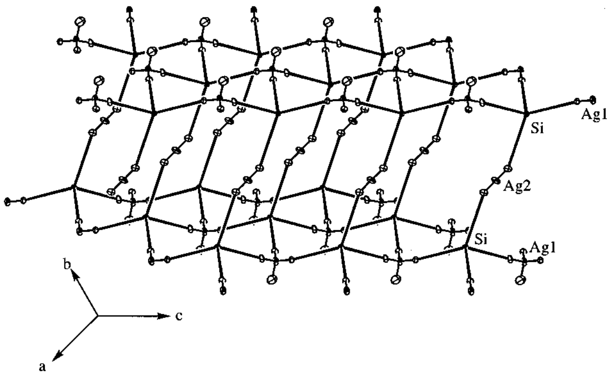

Figure 10. Two 3-connected layers linked in a "face-to-face" fashion in **3**. Oxygen atoms from the THF ligands are shown as being bonded to every Ag(1) atom. The Ag(3) atoms are omitted for clarity.

solvent interactions. The double layers in this structure are heavily interwoven such that each double layer is interpenetrated to some degree by four others.

Some disorder in the structure also exists in the vicinity of Ag(2). This disorder appears to result from two chemically unique CN−Ag−NC interactions. The Ag(2) atoms have a coordination number of 2 and a linear coordination geometry with relatively short Ag(2)−N(4) contacts (2.057(9) Å). A second environment for silver is represented by the Ag(3) positions, which have an occupancy of 18%, while Ag(2) has an occupancy of 82% (Figure 11). These silver atoms are three-coordinate (via an additional bonding interaction between Ag(3) and a neighboring PF_6^- ion, leading to a Ag(3)−F(10) bond length of 2.50(4) Å) and therefore experience a somewhat greater separation from the ligated nitrogen atoms (2.50(2) Å for Ag(3)−N(4); 2.42(2) Å for Ag(3)−N(4)*). The resulting N(4)−Ag(3)−N(4)* bond angle is 113.7(7)°.

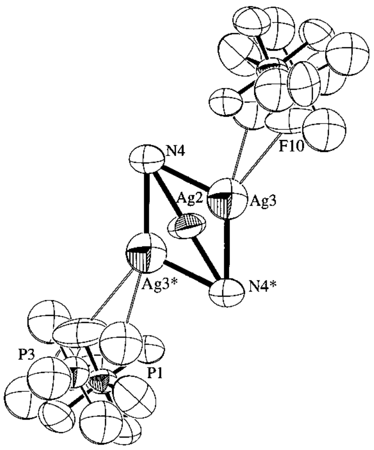

Figure 11. View of the environments about Ag(2) and Ag(3) in **3**.

The highly interpenetrated structure for **3** does not possess large free channels or pores. Consistent with this, the observed THF:benzene content is not changed by exposure of **3** to neat benzene for 4 h. Complex **3** is also quite air-sensitive, and analysis by TGA showed that the dichloromethane was lost between room temperature and 130 °C. The THF and benzene were lost at somewhat higher temperature, between 130 and 160 °C, presumably because these solvents are coordinated to silver in the structure. The latter desolvation was followed by an abrupt weight loss due to the decomposition of **1**. Thus, the molecules of **1** in **3** are more thermally labile than those in pure samples of **1**. Further evidence for this was found by heating a sample of **3** to 130 °C under vacuum for 30 min. According to ^1H NMR spectroscopy, the tetrahedral building block **1** had significantly decomposed by this treatment (by ca. 20%). Apparently, the PF_6^- anions in the structure react with the silane **1** at elevated temperatures.

Discussion

The tetrahedral silane building block **1** crystallizes with Ag^+ into two different lattices, depending on the anion and/or solvent system employed. The coordination networks **2** and **3** both possess 3-connected layers. In **2**, the six-membered rings in the layer are in an unusual envelope conformation, while the rings in the layers of **3** adopt a chair conformation. In both structures, one type of Ag center is incorporated into 3-connected layers, while a second type serves to interconnect layers via nitrile groups that protrude from the 3-connected layers. The main differences between the structures of **2** and **3** may be due largely to differences in the nature of the Ag−anion interactions. The triflate anion clearly plays a stronger role in binding Ag^+ ions, as in the formation of the triflate-bridged $Ag(\mu\text{-}O_3SCF_3)_2$-Ag groups. On the other hand, the PF_6^- anion in **3** appears to play a minor role in defining the framework structure. These differences in Ag−anion interactions also lead to different silver: silane ratios for the two structures.

It is of interest to compare **2** and **3** with $[Ag((4\text{-}C_6H_4CN)_4C)]$-$OTf{\cdot}3C_6H_6$,[3d] which possesses a 3-connected, undulating layer containing the ligand and Ag^+. In the latter structure, the Ag^+ centers are also coordinated to triflate and the remaining nitrile groups which extend from the layer are left uncoordinated. In $[Cu((4\text{-}C_6H_4CN)_4C)]BF_4{\cdot}x\text{PhNO}_2$,[1] the tetrahedral building block is linked by four-coordinate Cu(I) centers to form a diamond lattice. This structure possesses relatively large cavities without interpenetration, and the cavities are filled by more than 7.7 mol of solvent molecules.

Compounds **2** and **3** are clearly not very stable to air or the removal of solvent. However despite its loss of observable crystallinity (by PXRD), **2** exhibits behavior as a molecular sieve, in that the guest benzene solvent can be exchanged with free benzene (ca. 86% over 4 h) and benzene can be at least partially reincorporated into the structure after exhaustive removal of the original benzene of crystallization. In the latter experiment, 0.2 mol of benzene was taken up after 1 h and 1.1 mol of benzene was incorporated after 24 h. The *slow* uptake of solvent is perhaps consistent with the observed structure of **2**, which does not contain large, open channels. After reincorporation of benzene, the TGA trace for the material displayed the same overall appearance for loss of benzene.

Future publications will describe the use of **1** in the construction of coordination networks with other metal centers and will discuss the development of related tetrahedral silane building blocks.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. We thank Dr. Fred Hollander of the departmental X-ray facility (CHEXRAY) for determination of the crystal structures and Claus Lugmair for help with obtaining powder X-ray diffraction data.

Supporting Information Available: Listings of crystal data and data collection and refinement parameters, atomic coordinates, bond distances and angles, and anisotropic displacement parameters for **2** and **3** (24 pages). Ordering information is given on any current masthead page.

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