

Coordination Networks Based on Multitopic Ligands and Silver(I) Salts: A Study of Network Connectivity and Topology as a Function of Counterion

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We show that much like hydrogen bonding, Ag–N coordination bonds can be reliably used for the construction of supramolecular networks. From a solid-state structural study of silver(I) complexes of multitopic ligands, we describe coordination networks formed in the presence of the weakly coordinating triflate (CF₃SO₃[−]) counterion and the noncoordinating hexafluorophosphate (PF₆[−]) species. For complexes prepared with silver(I) triflate, counterion coordination is characteristic. Also, for the triflate complexes presented, ditopic ligands form one-dimensional, chainlike structures and tritopic ligands form 3-connected nets. A tetratopic ligand also forms a 3-connected net due to the triflate-capped silver(I) coordination. In contrast, more varied network topology is seen in complexes of ditopic ligands prepared with silver(I) hexafluorophosphate.

Introduction

The control of molecular organization in the solid state is an important theme of modern chemistry. It is in this regard that there is presently widespread activity in the area of supramolecular networks. In the construction of these networks, there is a preference for the use of directional intermolecular interactions such as hydrogen bonds,¹ metal–ligand coordination bonds,² and donor–acceptor interactions.³ This approach is based on the premise that if these interactions dominate the crystal field, then the solid-state structure should

follow from the directional preferences associated with these interactions. This points to the need for supramolecular interactions with reliable directional characteristics. Since the theoretical methods that would make these predictions are unavailable at the present time, a pragmatic approach is to identify recurrent relationships that exist between the molecular structure(s) and the solid-state structure. Such efforts have resulted in the identification of various bonding patterns associated with hydrogen-bonded networks.^{1d}

Coordination networks result from the binary combination of a metal and a multitopic ligand.⁴ Topologically, the molecules and atoms in these networks can be considered as points and the network connectivity can be described in terms of *p* and *q*, the connectivity of the ligand and metal, respectively.⁵ Considering the motif as a modular assembly of organic and metal units, the topology of the network is expected to follow from the geometry of its constituents. The structural motifs that result from these combinations can be related to and discussed in the context of solid-state structural prototypes by the replacement of the inorganic element or ion of a given symmetry and connectedness in the prototype with the multitopic organic module of identical symmetry and connectedness.⁶ Since the connectedness of the multitopic ligand is controlled by design via covalent synthesis, prediction of the network motif relies on the knowledge of the coordination characteristics of

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(3) (a) Hillier, A. C.; Ward, M. D. *Science* **1994**, *263*, 1261–1264. (b) Russel, V. A.; Etter, M. C.; Ward, M. D. *J. Am. Chem. Soc.* **1994**, *116*, 1941–1951.

(4) A multitopic ligand is one equipped with multiple coordination sites and, as a function of a rigid geometry, is unable to chelate to a metal center. This type of ligand should be contrasted with multidentate ligands such as ethylenediamine for which chelation is a common mode of binding.

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Table 1. Coordination Propensity of Silver(I) As Tabulated from a Search of the Cambridge Structural Database (90 Structures Analyzed)^a

coordination no. ^a	coordination geometry	no. of structures
2	linear	43
2	bent	3
3	trigonal planar	18
3	T-shaped	3
3	pyramidal	1
4	tetrahedral	13
4	trigonal pyramidal	8
4	square planar	1

^a No structures with a coordination number greater than four were observed.

the metal. In this context, we present structural studies of coordination networks derived from multitopic ligands and silver(I) salts.

Silver(I) is a soft metal center with a high affinity for soft nitrogen ligands.⁷ Many salts of silver(I) with counterions such as triflate (CF₃SO₃⁻), hexafluorophosphate (PF₆⁻), and tetrafluoroborate (BF₄⁻) are known to be soluble in organic solvents. The coordination number and geometry of silver can vary widely as revealed by structures in the Cambridge Structural Database (CSD, see Table 1).^{8,9} This prompts an important question: What are the factors that determine coordination number and hence influence network topology? In an effort to answer this question, we have initiated a study of coordination networks as a function of ligand topicity and counterion. Ligands used are multitopic aromatic skeleton functionalized with pyridine or nitrile groups (see Chart 1). The counterions chosen were triflate, which is known to weakly coordinate to various metal ions,¹⁰ and hexafluorophosphate, which is generally noncoordinating.¹¹

Experimental Section

General Procedures. All starting materials, unless otherwise indicated, were purchased from Aldrich Chemical Co.

(6) Structures recently prepared by this method include molecular analogues of the diamond, rutile, simple cubic, PtS, and the ThSi₂ structures. See (a) Robson, R.; Abrahams, B. F.; Batten, S. R.; Gable, R. W.; Hoskins, B. F.; Liu, J. *Supramolecular Architecture*; Bein, T., Ed., ACS Symposium Series 499, American Chemical Society: Washington, DC, 1992; Chapter 19. (b) Hoskins, B. F.; Robson, R.; Scarlett, N. V. *J. Chem. Soc., Chem. Commun.* **1994**, 2025–2026. (c) Abrahams, B. F.; Hoskins, B. F.; Michail, D. M.; Robson, R. *Nature* **1994**, 369, 727–729. (d) Gardner, G. B.; Venkataraman, D.; Moore, J. S.; Lee, S. *Nature* **1995**, 374, 792–795.

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(8) We have compiled a coordination geometry table of d-block transition metals and their ions from the structures contained in the Cambridge Structural Database. This table can be downloaded from the Internet as individual gif files from URL <http://www.sulfur.sc.siu.edu>. For the details of the search, see: Venkataraman, D.; Du, Y.; Wilson, S. R.; Hirsch, K. A.; Zhang, P.; Moore, J. S. *J. Chem. Educ.*, in press.

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(11) For a review of coordination propensities of hexafluorophosphate and tetrafluoroborate ions and their comparison to triflate, see: Beck, W.; Sünkel, K. *Chem. Rev.* **1988**, 88, 1405–1421.

and were used without further purification. 4,4',4'',4'''-Tetracyanotetraphenylmethane was synthesized according to established procedures.¹² For the crystallization experiments, all vials (16 × 65 mm) were soaked in a chromic acid bath for 24 h, washed with water and acetone, and dried in an air oven at 115 °C. Teflon-lined screw caps were used to seal the vials. Analytical grade solvents were obtained from commercial suppliers and were used without further purification. Silver(I) triflate and silver(I) hexafluorophosphate were stored in a desiccator with Drierite as the drying agent. An oven equipped with a programmable Eurotherm or Thermolyne temperature controller was used for heating and cooling. The samples were initially heated to 70 or 100 °C and were maintained at that temperature for 1–2 h before the start of the cooling ramp. The heating rate was set at 20 °C h⁻¹ for all samples. Cooling rates and crystallization protocol were optimized for each complex, and detailed procedures are described. A flowchart that outlines the general approach followed for crystal growth optimization is provided in the supporting information. Crystals with silver(I) hexafluorophosphate were stored in the dark as they were found to be sensitive to light, while no such precautions were necessary for crystals with silver(I) triflate. No special procedures were employed to exclude oxygen or moisture during crystallization.

The X-ray data were collected on a Syntex P2₁ or Enraf-Nonius CAD-4 diffractometer with Mo Kα (λ = 0.710 73 Å) as the incident radiation. Diffraction data were collected at ambient temperatures unless otherwise indicated. Accurate cell dimensions were obtained from the setting angles of 25 carefully centered reflections using a least-squares procedure. The intensity data were reduced by profile analysis and corrected for Lorentz–polarization and absorption effects, if necessary.¹³ Scattering factors and anomalous dispersion terms were taken from standard tables.¹⁴ The structure solutions were obtained by Patterson or direct methods using SHELXTL PLUS and were refined using full-matrix least-squares analysis on all reflections, based on F_o², with SHELXL-93 on a Silicon Graphics Indigo RS 4000 workstation.¹⁵ All cell parameters were checked for higher metric symmetry using the LePage (ver. Oct 3, 1990),¹⁶ XPREP,¹⁷ and/or PLATON programs.¹⁸ All structures were checked for any missing symmetry using CALC MISSYM of PLATON.

An X-ray powder diffraction pattern of **1** was taken on a Rigaku-Dmax powder diffractometer and for **12** on a Guinier camera with Cu Kα₁ (λ = 1.5405 Å) as the incident radiation. The powder X-ray diffraction (PXRD) data (ASCII format) obtained from the Rigaku-Dmax diffractometer was converted into 2cam format (Cerius² readable)¹⁹ and were compared with the theoretical patterns generated by the Cerius² program on a Silicon Graphics Indigo RS 4000 workstation. For the pattern obtained with a Guinier camera, theoretical intensities were calculated using the Lazy Pulverix program²⁰ and were compared with the photographic pattern.

[Ag(1,4-pyrazine)_{1.5}CF₃SO₃] (1). A solution of silver(I) triflate (17.2 mg, 0.07 mmol) in acetone (2 mL) was added to a solution of 1,4-pyrazine (5.0 mg, 0.06 mmol) in acetone (2 mL) in a clean vial with a Teflon-lined screw cap. A white precipitate formed. The sealed vial was heated to 85 °C in a hot-water bath producing a clear solution. The resulting solution was filtered while hot to remove insoluble matter

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(16) Le Page, Y. *J. Appl. Cryst.* **1982**, 15, 255–259.

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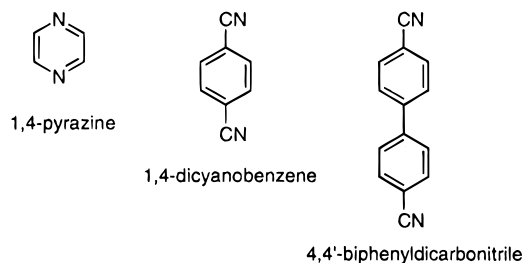
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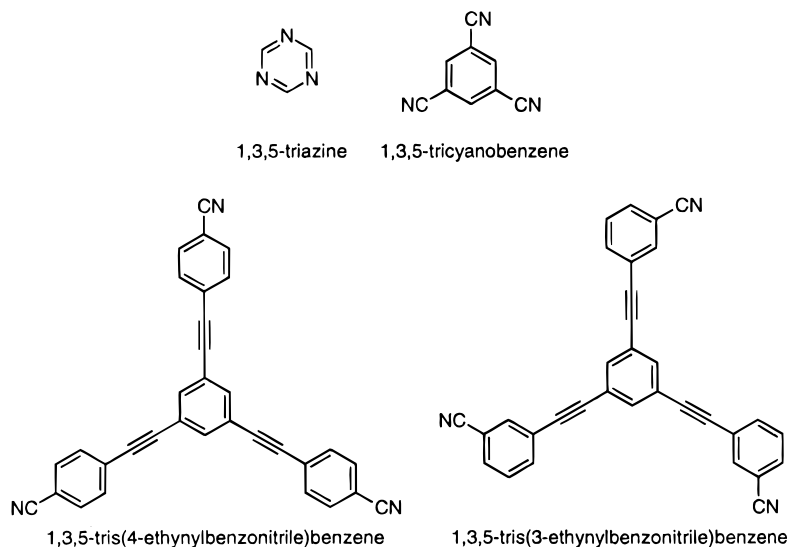
(20) Yvon, K.; Jeitschko, W.; Parthe, E. *J. Appl. Cryst.* **1977**, 10, 73–74.

Chart 1

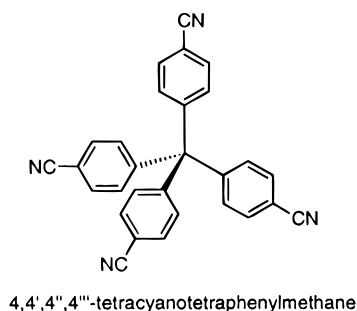
Ditopic ligands



Tritopic ligands



Tetratopic ligand



through a Whatman No. 50 filter paper into another vial with a Teflon-lined cap. The clear solution turned turbid on cooling. The resulting mixture was heated in an oven to 70 °C, and the homogeneous solution was cooled to room temperature at 1.2 °C h⁻¹. Colorless, long needles suitable for X-ray data collection resulted. The PXRD pattern of the bulk sample matched with the calculated pattern from the single-crystal X-ray data.

[Ag(1,4-pyrazine)](PF₆)_{0.5}(OH)_{0.5} (2).²¹ A solution of silver(I) hexafluorophosphate (1 mL, 0.01 M) in methanol–water (1:1) was added to a solution of 1,4-pyrazine (1 mL, 0.01 M) in methanol–water (1:1) in a vial with a Teflon-lined cap. This resulted in the formation of a white precipitate. Four such samples were prepared and to each of these, methanol–water (1:1) was added such that the final volumes were 3, 4, 5, and 6 mL. The sample vials were heated to 70 °C and cooled to

room temperature at the rate of 1.0 °C h⁻¹. On cooling, colorless needles were obtained along with a brown precipitate at the bottom of each of the vials. Suitable crystals for X-ray analysis were removed from the vial whose final volume was 5 mL.

[Ag(1,3,5-triazine)CF₃SO₃]₂·H₂O (8). A solution of 1,3,5-triazine (10.0 mg, 0.10 mmol) and silver(I) triflate (30.3 mg, 0.10 mmol) in acetone (4 mL) was heated to 70 °C in a sealed vial in an oil bath. The warm solution was filtered into a vial through a Whatman No. 50 filter paper. The vial was sealed with a Teflon-lined screw cap and was reheated to 80 °C. Slow cooling to ambient temperature at the rate of 1.2 °C h⁻¹ resulted in X-ray-quality single crystals.

[Ag(1,3,5-tris(4-ethynylbenzonitrile)benzene)-CF₃SO₃]₂·2C₆H₆ Polymorph (B) (12). A solution of silver(I) triflate (6.7 mg, 0.03 mmol) in benzene (2 mL) was very slowly added to a solution of 1,3,5-tris(4-ethynylbenzonitrile)benzene (10.6 mg, 0.02 mmol) in benzene (1 mL) in a clean vial with a Teflon-lined screw cap. The addition resulted in the formation of a white precipitate. The capped vial with the precipitate was heated to 100 °C in an oven and cooled to room temper-

(21) Recently, Ciani and co-workers reported the crystal structure of [Ag(1,4-pyrazine)₂](PF₆)₂. Undulating 2-D sheets constitute this structure. See: Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *Inorg. Chem.* **1995**, *34*, 5698–5700.

Table 2. Crystal Data and Structure Refinement Parameters for 1, 2, 8, 12, and 14

formula	C ₇ H ₆ N ₃ O ₄ F ₃ SAg (1)	C ₄ H ₄ N ₂ O _{0.5} F ₃ P _{0.5} Ag (2)	C ₄ H ₃ N ₃ O ₄ F ₃ SAg (8)	C ₄₆ H ₂₇ N ₃ O ₃ F ₃ SAg (12)	C ₅₁ H ₃₇ N ₄ O ₃ F ₃ SAg (14)
molecular weight	377.08	240.50	354.02	866.64	950.80
crystal system	triclinic	tetragonal	orthorhombic	monoclinic	triclinic
space group	$P\bar{1}$ (2)	$I4_1/amd$ (141)	$P2_1/cn$ (33)	$P2_1/c$ (14)	$P\bar{1}$ (2)
<i>a</i> (Å)	7.305(2)	7.138(10)	8.222(1)	5.970(3)	12.646(3)
<i>b</i> (Å)	9.037(4)	7.138(10)	9.441(2)	31.470(2)	14.222(3)
<i>c</i> (Å)	10.504(5)	30.212(6)	11.932(2)	21.200(13)	14.808(4)
α (deg)	98.73(2)	90.00	90.00	90.00	64.94(2)
β (deg)	106.79(2)	90.00	90.00	90.53(5)	73.62(2)
γ (deg)	111.84(2)	90.00	90.00	90.00	77.63(2)
<i>V</i> (Å ³)	589.4(4)	1539.3(4)	926.2(3)	3982.0(4)	2300.8(10)
<i>Z</i>	4	8	4	4	2
<i>d</i> _{calc} (g·cm ⁻³)	2.125	2.386	2.539	1.441	1.372
θ range (deg)	2.5–24.4	3.5–25.4	2.7–26.0	2.6–22.8	1.7–24.0
no. of rflns collected	2002 [<i>R</i> (int) = 0.024]	2908 [<i>R</i> (int) = 0.030]	1970 [<i>R</i> (int) = 0.029]	7044 [<i>R</i> (int) = 0.082]	7420 [<i>R</i> (int) = 0.028]
no. of independent rflns	1941 [1688 obs, <i>I</i> > 2 σ]	422 [367 obs, <i>I</i> > 2 σ]	1837 [1738 obs, <i>I</i> > 2 σ]	5070 [1313 obs, <i>I</i> > 2 σ]	7113 [6376 obs, <i>I</i> > 2 σ]
no. of rflns refined	1941	422	1837	5070	7113
<i>a</i> , <i>b</i> ^a	0.0703, 0.9840	0.0340, 3.4291	0.0548, 1.1131	0.1092, 0.0000	0.0543, 1.4984
data/restraints/parameters	1941/0/170	422/0/45	1837/1/158	5070/72/216	7113/34/521
GOF ^b (all data)	1.138	1.234	1.096	0.630	1.059
final <i>R</i> indexes (<i>F</i> > 4 σ) ^c	<i>R</i> 1 = 0.0409, <i>wR</i> 2 = 0.1135	<i>R</i> 1 = 0.0261, <i>wR</i> 2 = 0.0709	<i>R</i> 1 = 0.0325, <i>wR</i> 2 = 0.0840	<i>R</i> 1 = 0.0733, <i>wR</i> 2 = 0.1836	<i>R</i> 1 = 0.0337, <i>wR</i> 2 = 0.0874
<i>R</i> indexes (all data)	<i>R</i> 1 = 0.0497, <i>wR</i> 2 = 0.1199	<i>R</i> 1 = 0.0319, <i>wR</i> 2 = 0.0752	<i>R</i> 1 = 0.0346, <i>wR</i> 2 = 0.0894	<i>R</i> 1 = 0.2084, <i>wR</i> 2 = 0.2181	<i>R</i> 1 = 0.0417, <i>wR</i> 2 = 0.0921
largest diff peak (e Å ⁻³)	0.52	0.35	0.45	0.90	0.45

^a Weights (*w*) used in the refinement are defined as $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (\max(F_o^2, 0) + 2F_c^2)/3$. ^b Goodness of fit (GOF) = $[\sum(w|F_o^2 - F_c^2|)^2/(n - p)]^{1/2}$, where *n* is the number of reflections and *p* is the number of parameters. ^c $R1 = \sum(|F_o - F_c|)/\sum|F_o|$ and $wR2 = [\sum(w|F_o^2 - F_c^2|)^2/\sum w|F_o^2|]^{1/2}$.

ature at the rate of 1.2 °C h⁻¹. The heating/cooling cycles were repeated four times yielding complete conversion of previously reported polymorph A^{6d} to polymorph B. This procedure has been reproduced several times. After final cooling, light yellow crystals were obtained, and those suitable for X-ray analysis were selected. The PXRD pattern of the bulk sample matched with the calculated pattern from the single-crystal X-ray data.

[Ag(4,4',4'',4'''-tetracyanotetraphenylmethane)CF₃SO₃]-3C₆H₆ (14). To a solution of 4,4',4'',4'''-tetracyanotetraphenylmethane (2.6 mg, 0.06 mmol) in benzene (1.5 mL) was added silver(I) triflate (1.5 mg, 0.05 mmol) in a clean vial with a Teflon-lined screw cap. The addition resulted in the formation of a white precipitate. The sealed vial was then heated in an oven to 100 °C and cooled to room temperature at the rate of 1.2 °C h⁻¹. On cooling, colorless, double-pyramidal crystals were obtained and selected for X-ray analysis.

Results

In this section, the stoichiometry of the metal–ligand complex is presented as M_{*n*}L_{*m*}. Table 2 summarizes the crystallographic details of the complexes described here. Table 3 shows the coordination characteristics of silver(I) in all of the complexes of the multitopic ligands with silver(I) triflate and silver(I) hexafluorophosphate. References for the structures that have appeared previously in the literature are provided in Table 3.

Ladder Structure of [Ag(1,4-pyrazine)_{1.5}CF₃SO₃] (1). The stoichiometry of the resultant metal–ligand complex of 1,4-pyrazine and silver(I) is ML_{1.5}. The structure consists of infinite chains of alternating 1,4-pyrazine molecules and silver(I) ions with each chain linked to another by 1,4-pyrazine bridges that form the rungs of a double-stranded “ladder-type” structure (Figure 1a) much like that of antimony trioxide (Sb₂O₃; valentinite).²² The chains run parallel to the *a*-axis. The 1,4-pyrazine units on the chain stack face-to-face at a distance of 3.55 Å along [0 –1 1]. The plane of the 1,4-

pyrazine bridges are at 77.8° to the plane of the poles of the ladder.

Silver(I) is four-coordinate and adopts a saw-horse geometry bonding to three nitrogens of 1,4-pyrazine and an oxygen of triflate as shown in Figure 1b. The N–Ag(1) bond distances are 2.246 Å (N1), 2.312 Å (N2), and 2.460 Å (N3) and the N–Ag(1)–N bond angles are 173.2° and 87.3°. The Ag(1)–O bond distance is 2.590 Å. The structure does not contain any cavities.

Infinite Chain Structure of [Ag(1,4-pyrazine)]-(PF₆)_{0.5}(OH)_{0.5} (2).²¹ The stoichiometry of the resultant complex with respect to 1,4-pyrazine and silver(I) is ML. The structure consists of two sets of infinite chains of alternating 1,4-pyrazine and silver(I) units (Figure 2a). The chains in these two sets are orthogonal running parallel to the *a* and *b* axes. Parallel chains stack such that the 1,4-pyrazine molecules are face-to-face at 3.56 Å with no offset along the axis (*a* or *b*) perpendicular to the chain axis. Along the stacking axis, Ag–Ag distances of 3.57 Å are observed. This structure may be compared to the double-stranded chain structure of (Si₄O₁₁)_{*n*}^{6*n*-} observed in Na₂ZrSi₄O₁₁ (vlasovite).²³ The hexafluorophosphate ion occupies space created between the two sets of chains. Of the eight hexafluorophosphate ions that were required in the unit cell, only four were identified from the Fourier difference map. On the basis of the thermal ellipsoids and *R*₁ value, residual electron densities that appeared in the Fourier difference map were modeled as disordered oxygen atoms, presumably of hydroxide ions. The chemical reaction that yielded the hydroxide ion is unknown. It is presumed that the hydrolysis of the hexafluorophosphate ion might have occurred since crystal growth involved heating AgPF₆ in methanol and water to elevated temperatures. No conclusive support for this

(22) See ref 5, p 711.

(23) See ref 5, p 817.

Table 3. Summary of the Crystal Structures of Coordination Networks Showing the Coordination Characteristics of Silver(I) and the Crystallization Conditions

structure	crystallization solvent	coordination geometry of Ag(I)	atoms/groups in coordination sphere	coord. no.	structure type	ref. ^a
[Ag(1,4-pyrazine) _{1.5} CF ₃ SO ₃] (1)	acetone	saw-horse	N, N, N, OTf	4	(2,3)-connected ladder structure with bridging 1,4-pyrazine molecules	A
[Ag(1,4-pyrazine)](PF ₆) _{0.5} (OH) _{0.5} (2)	methanol/water	linear	N, N	2	chains	A
[Ag(1,4-dicyanobenzene)(CF ₃ SO ₃)(H ₂ O) _{0.5}] (3)	benzene	trigonal pyramidal	N, N, OTf, OH ₂	4	1-D, 2-connected infinite chains bridged by a water molecule	32a
[Ag(1,4-dicyanobenzene)(H ₂ O)]PF ₆ (4)	toluene	saw-horse	N, N, OH ₂ , OH ₂	4	1-D, 2-connected infinite chains bridged by two water molecules	32a
[Ag(4,4'-biphenyl)dicyanitrile](CF ₃ SO ₃)-C ₆ H ₆ (5)	benzene	T-shaped	N, N, OTf	3	1-D, 2-connected infinite chains	7d
[Ag(4,4'-biphenyl)dicyanitrile] ₂ PF ₆ (A) (6)	toluene	tetrahedral	N, N, N, N	4	interpenetrated 4-connected diamondoid nets	7d
[Ag(4,4'-biphenyl)dicyanitrile] ₂ PF ₆ (B) (7)	ethanol	tetrahedral	N, N, N, N	4	interpenetrated 4-connected diamondoid nets	7d
[Ag(1,3,5-triazine)(CF ₃ SO ₃)]·H ₂ O (8)	acetone	trigonal pyramidal	N, N, N, OTf	4	three-dimensional (10,3) nets	A
[Ag(1,3,5-tricyanobenzene)(CF ₃ SO ₃)] (9)	benzene	trigonal pyramidal	N, N, N, OTf	4	3-connected graphitic sheets	6d
[Ag(1,3,5-tricyanobenzene)(7 ² -C ₇ H ₉)]PF ₆ (10)	toluene	distorted trigonal pyramidal	N, N, N, toluene	4	undulating 3-connected graphitic sheets	32b
[Ag(1,3,5-tris(4-ethynylbenzonitrile)benzene)CF ₃ SO ₃]-2C ₆ H ₆ (A) (11)	benzene	trigonal pyramidal	N, N, N, OTf	4	interpenetrated 3-connected ThSi ₂ -type nets	6d
[Ag(1,3,5-tris(4-ethynylbenzonitrile)benzene)CF ₃ SO ₃]-2C ₆ H ₆ (B) (12)	benzene	trigonal pyramidal	N, N, N, OTf	4	interpenetrated 3-connected graphitic sheets	A
[Ag(1,3,5-tris(3-ethynylbenzonitrile)benzene)CF ₃ SO ₃]-2C ₆ H ₆ (13)	benzene	trigonal pyramidal	N, N, N, OTf	4	3-connected annulene-type sheets	7c
[Ag(4,4',4'',4'''-tetracyanotetraphenylmethane)CF ₃ SO ₃]-3C ₆ H ₆ (14)	benzene	distorted tetrahedral	N, N, N, OTf	4	undulating (6,3) nets	A

^a A = present work.

counterion composition was obtained from combustion analyses. The equatorial fluorine atoms in the hexafluorophosphate ions were modeled as being disordered. The two-coordinate silver(I) ions adopt a linear geometry, bonding to the nitrogens of the 1,4-pyrazine ligand (Figure 2b). The N–Ag(1) bond distance is 2.191 Å and the N–Ag(1)–N bond angle is 180.0°. The resultant structure does not have open channels.

Complex (10,3) Net Structure of [Ag(1,3,5-triazine)CF₃SO₃]-H₂O (8). The stoichiometry of the complex formed from 1,3,5-triazine and silver(I) triflate is ML. The structure consists of three-dimensional, (10,3) nets with alternating 1,3,5-triazine and silver(I) units (Figure 3a). The 1,3,5-triazine ligands can be divided into two sets in which the planes of the rings in the first set are approximately perpendicular to the planes of the rings of the other.

It is rather intriguing that the structure does not conform to one of the common prototypic 3-connected structures: two-dimensional AlB₂ or three-dimensional ThSi₂. Molecular models of hypothetical AlB₂- and ThSi₂-type nets constructed from 1,3,5-triazine and silver(I) ions indicate severe intermolecular nonbonded contacts between hydrogen atoms. Presumably, the observed structure is adopted to relieve this strain. Indeed, it is possible to derive the observed 3-D structure from the simple 2-D graphitic (AlB₂) net. To perform this transformation, a 1,3,5-triazine unit in the hypothetical graphitic net can be pulled out of the plane by the cleavage of two of the three Ag–N bonds. As the strand is pulled up, it forms a helix by making bonds with the silver units in the adjacent layer. Following this conjecture, the structure can be construed as a packing of helices as shown in Figure 3b.

Silver(I) is four-coordinate and adopts a trigonal-pyramidal geometry, forming bonds to the nitrogens of 1,3,5-triazine units and an oxygen of triflate (see Figure 3c). The N–Ag bond distances are 2.312, 2.342, and 2.430 Å. The N–Ag–N bond angles are 146.8°, 113.8°, and 98.8°. Triflate counterions are located 2.67 Å from silver(I) and occupy cavities which are ca. 6.5 Å in diameter. A molecule of water also occupies this cavity. Even though the stoichiometry observed from combustion analysis indicates two water molecules, the second molecule of water could not be located from the Fourier difference map.

Nonporous, Interpenetrated, (6,3) AlB₂-Type Net Structure of [Ag(1,3,5-tris(4-ethynylbenzonitrile)-benzene)CF₃SO₃]-2C₆H₆ (Polymorph B) (12). Following the procedure detailed in the Experimental Section, a second polymorph of the ML complex between 1,3,5-tris(4-ethynylbenzonitrile)benzene (TEB) with silver(I) triflate has been characterized. The structure consists of undulating (6,3) nets with alternating TEB and silver(I) units. The large, tritopic TEB molecules create void space of ca. 22 Å in a single (6,3) net (see Figure 4). Five more nets interpenetrate to fill the void space. Interpenetration occurs such that the aromatic units stack face-to-face at a distance of 3.56 Å with an offset of 28.7°. Silver(I) is four-coordinate and adopts a distorted tetrahedral geometry bonding to three nitriles of TEB and an oxygen of triflate. The N–Ag distances are 2.261, 2.280, and 2.300 Å. The N–Ag–N angles are 110.8°, 114.8°, and 122.7°. The Ag–O distance is 2.49 Å.

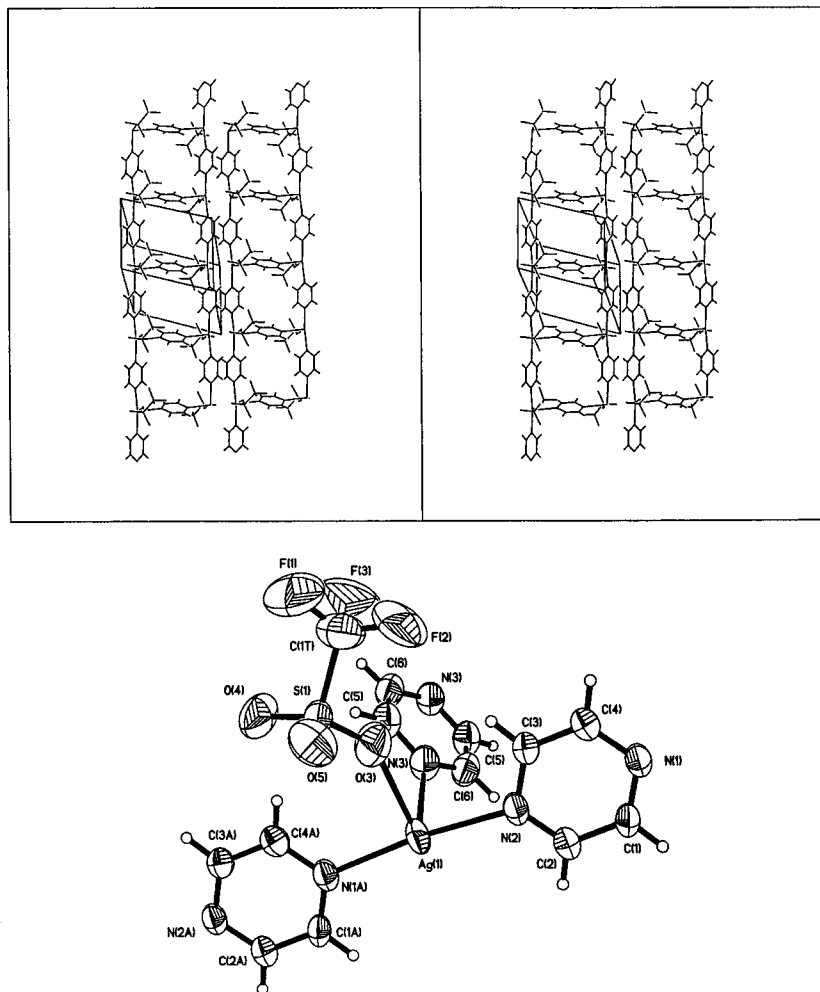


Figure 1. (a, top) Stereoview showing the chains that run along the a axis in the $[\text{Ag}(\text{1,4-pyrazine})_{1.5}\text{CF}_3\text{SO}_3]$ complex. The stacking of the 1,4-pyrazine ring along $[0 -1 1]$ can also be seen. (b, bottom) An ORTEP (50% probability ellipsoids) showing the coordination sphere of silver(I) in the $[\text{Ag}(\text{1,4-pyrazine})_{1.5}\text{CF}_3\text{SO}_3]$ complex. Silver(I) adopts a sawhorse geometry. Selected bond distances and angles: $\text{N1(A)}-\text{Ag}(1) = 2.246 \text{ \AA}$, $\text{N2}-\text{Ag}(1) = 2.312 \text{ \AA}$, $\text{N3}-\text{Ag}(1) = 2.460 \text{ \AA}$, $\text{O}(3)-\text{Ag}(1) = 2.590 \text{ \AA}$, $\angle\text{N1(A)}-\text{Ag}(1)-\text{N2} = 173.2^\circ$ and $\angle\text{N2}-\text{Ag}(1)-\text{N3} = 87.3^\circ$.

The triflate counterion was modeled as being disordered over two sites. Coordinates of two benzene molecules (2 mol of benzene/mol of TEB) were located from the Fourier difference map. One of the benzene molecules was modeled as being disordered over three sites. The other benzene molecule is well ordered and occupies the space between the layers. This structure is not porous as a result of self-inclusion. This polymorph is more stable and dense than the previously reported polymorph A.^{6d}

3-Connected Undulating Sheets of $[\text{Ag}(4,4',4'',4'''\text{-tetracyanotetraphenylmethane})\text{CF}_3\text{SO}_3] \cdot 3\text{C}_6\text{H}_6$ (14). The stoichiometry of the resultant complex with respect to 4,4',4'',4'''-tetracyanotetraphenylmethane and silver(I) is ML. The structure consists of undulating 2-D, 3-connected nets with alternating 4,4',4'',4'''-tetracyanotetraphenylmethane and silver(I) units (see Figure 5a). Silver(I) is four-coordinate and adopts a distorted tetrahedral coordination as shown in Figure 5b. Coordination to three of the four nitriles of 4,4',4'',4'''-tetracyanotetraphenylmethane and an oxygen of the triflate counterion is observed. *The remaining nitrile is left uncoordinated.* The cavities that are created in a single net are filled by the uncoordinated nitrile from the adjacent layer. Six benzene molecules (3 mol of benzene/mol of 4,4',4'',4'''-tetracyanotetraphenylmethane)

were located in the unit cell, and they occupy the space created between the layers. The N-Ag distances are 2.279, 2.241, and 2.193 Å. The N-Ag-N angles are 99.8°, 108.2°, and 126.0°. The Ag-O distance is 2.362 Å.

Discussion

The coordination polyhedron of a metal is generally influenced by the counterion, solvent, and topicity of the ligands. Noncoordinating counterions provide an advantage in that the metal is free to fill its coordination sphere with network-forming ligands. Since the coordination sphere of many metal ions is flexible,^{8,9} a large number of possibilities exists for the network for a given ligand topicity. However, if subtle constraints are applied to the coordination number of the metal by capping its coordination sphere with a coordinating counterion, then the predictability of the final network should increase. In the present case, for silver(I), coordination numbers beyond four are rare (see Table 1).²⁴ Hence, if the triflate counterion were to occupy a coordination site, then the residual coordination number, defined as the number of network ligands that could

(24) For a rare example of six-coordinate silver(I), see ref 2d.

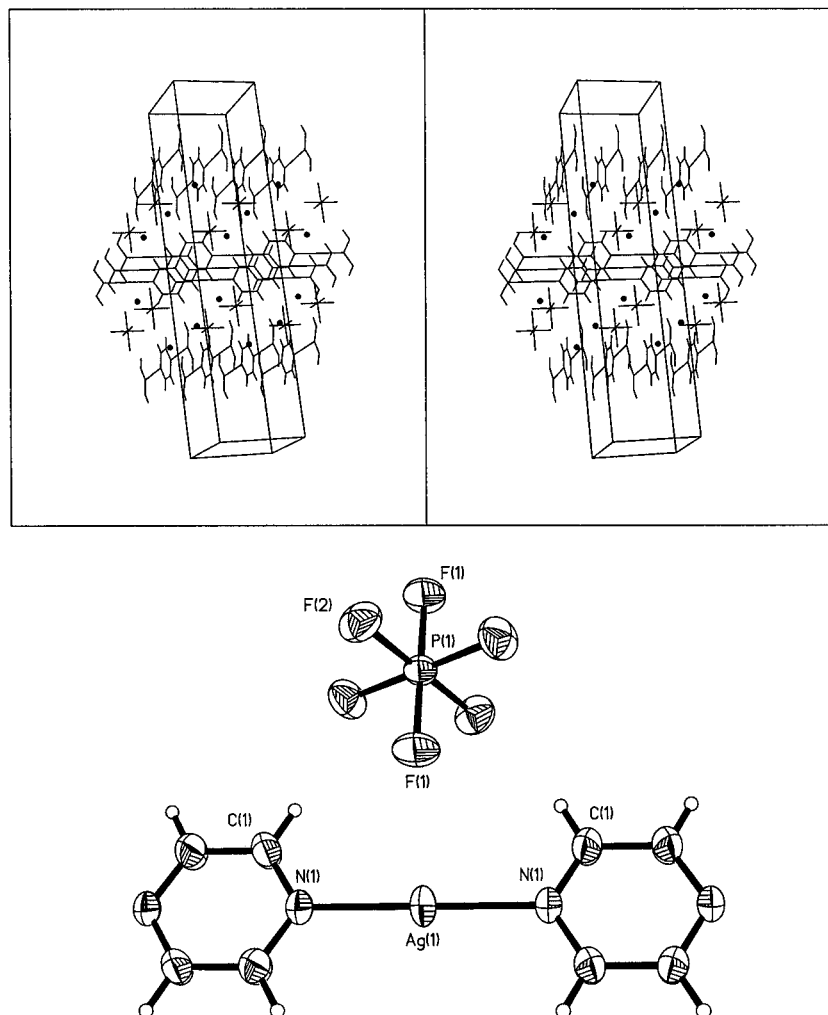


Figure 2. (a, top) Stereoview showing the chains that run along the *a* and *b* axes in the $[\text{Ag}(1,4\text{-pyrazine})](\text{PF}_6)_{0.5}(\text{OH})_{0.5}$ complex. The oxygen atoms of presumably the hydroxide ions are shown as shaded circles. The equatorial fluorine atoms of the hexafluorophosphate ions shown are the average atomic positions as they were modeled as being disordered. Short Ag–Ag contacts of 3.57 Å are observed along the stacking directions. The structure can be compared to the double-stranded chains of $(\text{Si}_4\text{O}_{11})_n^{6n-}$ observed in $\text{Na}_2\text{ZrSi}_4\text{O}_{11}$ (vlasovite). (b, bottom) An ORTEP (50% probability ellipsoids) showing the coordination sphere of silver(I) in the $[\text{Ag}(1,4\text{-pyrazine})](\text{PF}_6)_{0.5}(\text{OH})_{0.5}$ complex. Silver(I) adopts a linear geometry. Selected bond distances and angles: N1–Ag(1) = 2.191 Å and $\angle\text{N1–Ag(1)–N1} = 180^\circ$.

enter the coordination sphere of silver(I), is reduced to a maximum of three.²⁵ Thus, the network may achieve a connectedness of two or three only.²⁶ This reduces the number of possible topologies for the network for a given ligand topicity. This hypothesis has been tested through comparison of networks formed with a weakly coordinating counterion (triflate) to those involving a noncoordinating counterion (hexafluorophosphate).

It can be seen from Table 3, that in all of the triflate complexes, the counterion is present in the coordination sphere of silver(I).²⁷ Given this constraint on the metal's coordination sphere, it is of interest to see whether the topicity of the ligand can dictate network connectivity. The ligands considered are di-, tri-, and tetra-topic with geometries that are linear, trigonal planar, and tetrahedral, respectively (see Chart 1). Of the three complexes of linear ligands with silver(I) triflate presented,

the basic network motif observed for two of them (complexes **3** and **5**) is a 2-connected, infinite, ML chain. Silver(I) coordinates to two nitrogens of the ditopic ligands and an oxygen of triflate.²⁸ For complex **3**, a molecule of adventitious water bonds to silver(I) (see Figure 6a). Water serves to bridge neighboring chains in this structure. A molecule of benzene (crystallization solvent) is bound weakly to silver(I) in **5** (see Figure 6c). An exception to the trend of simple ML chains is the structure of $[\text{Ag}(1,4\text{-pyrazine})_{1.5}(\text{CF}_3\text{SO}_3)]$ (**1**). In this complex, in addition to the two pyrazine molecules and triflate counterion, another molecule of pyrazine enters the coordination sphere of silver(I) and bridges the chains, resulting in a stoichiometry of $\text{ML}_{1.5}$ (see Figure 1a,b). Despite the different stoichiometries observed, these networks formed from ditopic ligands and silver(I) triflate are all one-dimensional.²⁹

(25) It should be noted that additional steric constraints may also be introduced by the coordinating counterion.

(26) If only one ligand enters the coordination sphere, a network solid will not result.

(27) The use of noncoordinating solvents such as benzene usually avoids the competition from the solvent to enter into the coordination sphere of the metal.

(28) A linear chain structure consisting of alternating pyrazine and silver(I) units with a coordinating nitrate ion was reported by Vranka and Amma. See ref 7a.

(29) A three-dimensional, diamondoid network of 4,4'-bipyridine and silver(I) triflate crystallized from isopropyl alcohol/acetone has been reported. See ref 7b.

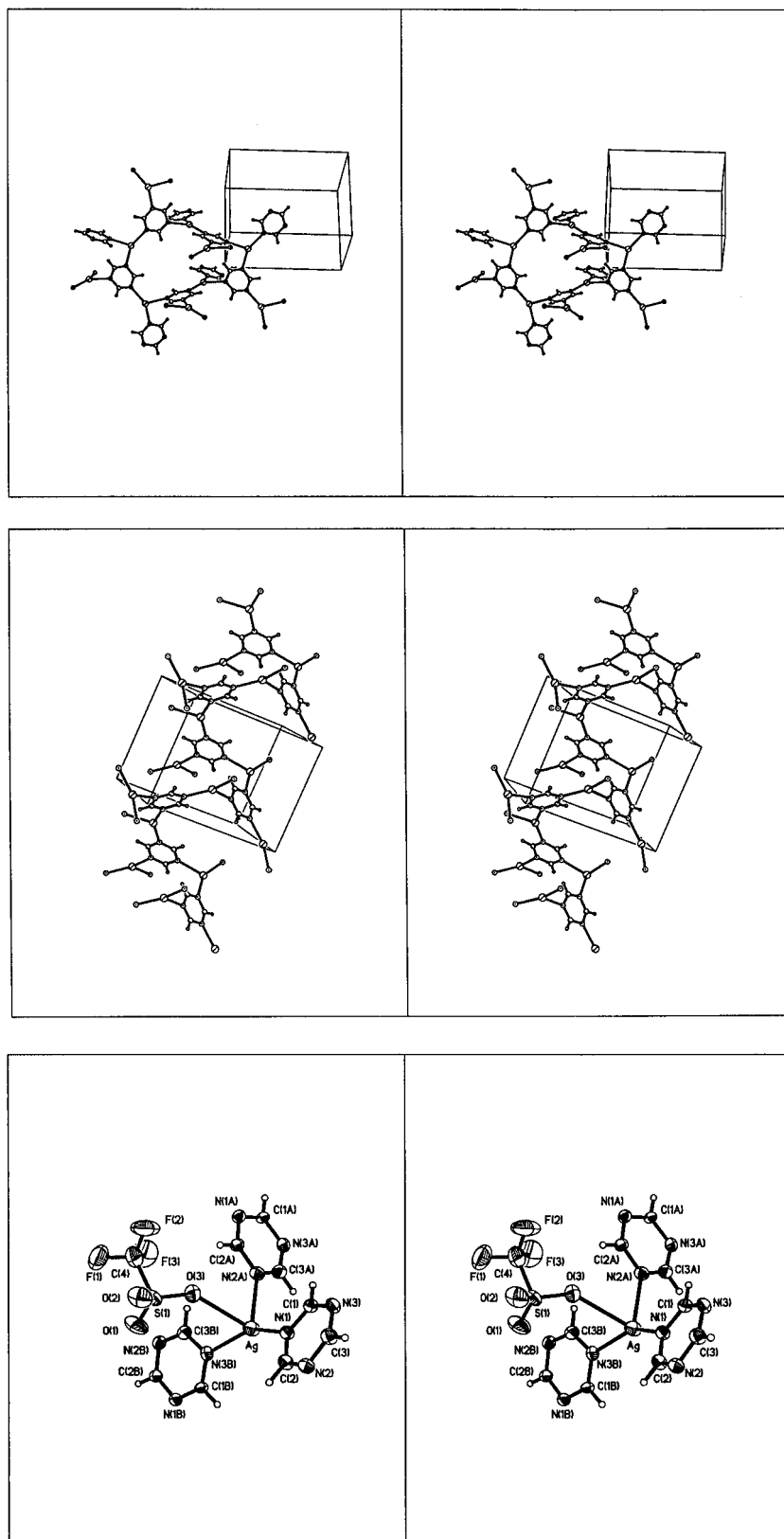


Figure 3. (a, top) Stereoview showing the (10,3) net in the structure of $[\text{Ag}(1,3,5\text{-triazine})\text{CF}_3\text{SO}_3]\cdot\text{H}_2\text{O}$. A triflate ion occupies the cavity. (b, middle) Stereoview showing the 3/1 helical chains in the structure of $[\text{Ag}(1,3,5\text{-triazine})\text{CF}_3\text{SO}_3]\cdot\text{H}_2\text{O}$. The packing of these helices and bonding between them constitutes the observed structure. As indicated by molecular modeling, this packing is presumed to be driven by relief of unfavorable steric interactions in the hypothetical graphitic or ThSi_2 -type nets. (c, bottom) Stereoview of an ORTEP (50% probability ellipsoids) showing the coordination sphere of silver(I) in the structure of $[\text{Ag}(1,3,5\text{-triazine})\text{CF}_3\text{SO}_3]\cdot\text{H}_2\text{O}$. Silver(I) adopts a trigonal-pyramidal geometry with the three nitrogen atoms in the basal plane and the oxygen of the triflate in the axial position. Selected bond distances and angles: $\text{N1}-\text{Ag} = 2.312 \text{ \AA}$, $\text{N2}-\text{Ag} = 2.342 \text{ \AA}$, $\text{N3}-\text{Ag} = 2.342 \text{ \AA}$, $\text{Ag}-\text{O}(1) = 2.67 \text{ \AA}$, $\angle\text{N1}-\text{Ag}-\text{N2} = 113.7^\circ$ and $\angle\text{N2}-\text{Ag}-\text{N3} = 98.8^\circ$.

In the case of the complexes of the tritopic ligands with silver(I) triflate, the observed networks are all

3-connected. Silver(I) is coordinated to three nitrogens of the tritopic ligand and an oxygen of triflate. The

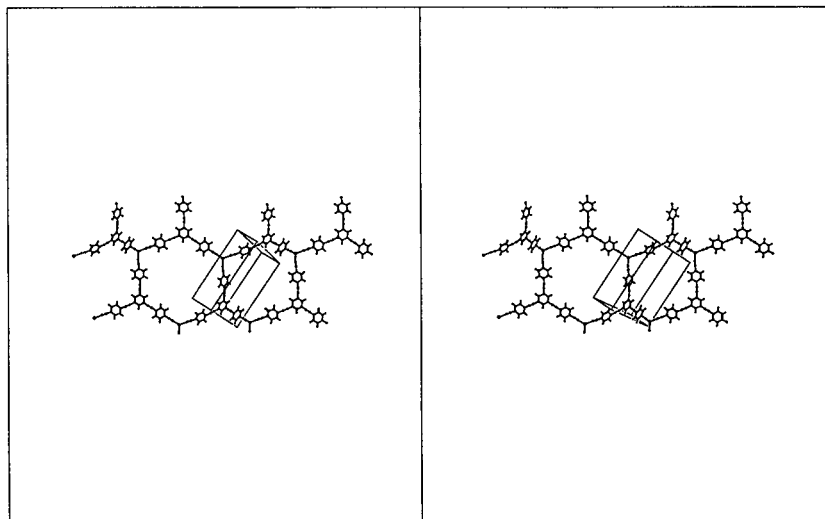


Figure 4. Stereoview showing a single undulating (6,3) net from the crystal structure of $[\text{Ag}(\text{1,3,5-tris(4-ethynylbenzonitrile)benzene})\text{CF}_3\text{SO}_3] \cdot 2\text{C}_6\text{H}_6$ (B). Five more nets interpenetrate to fill the ca. 22 Å space that is created in this net.

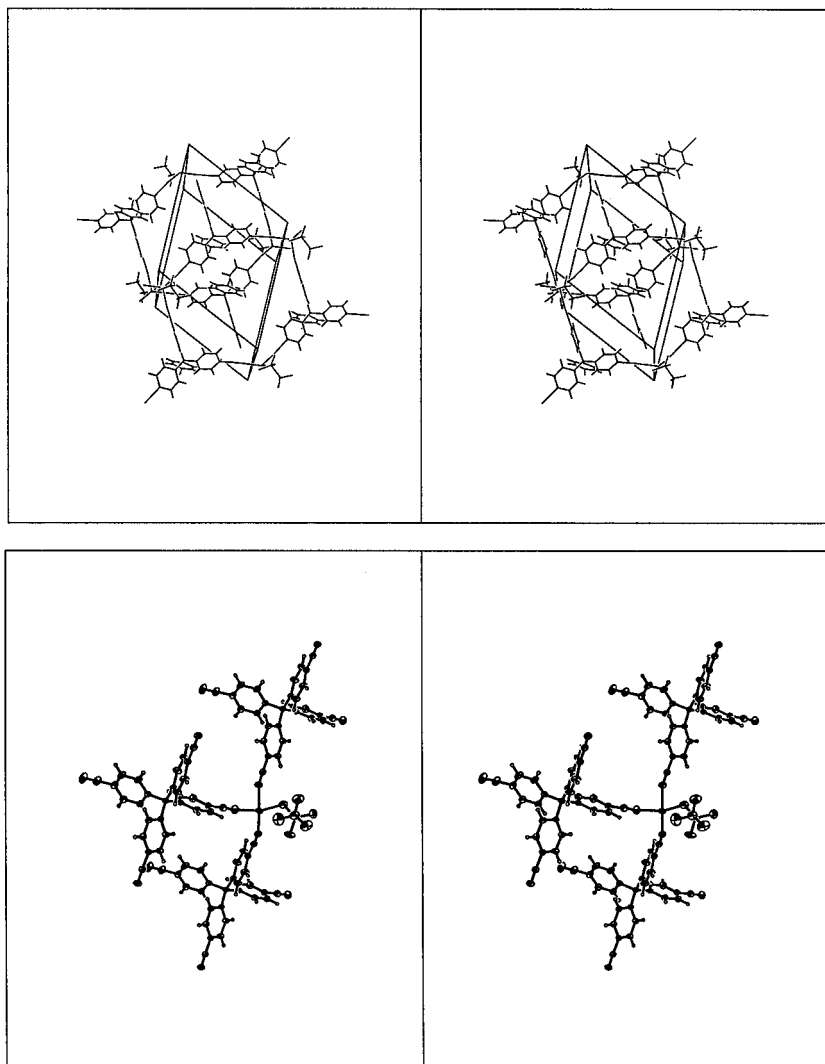


Figure 5. (a, top) Stereoview showing the undulating 3-connected net in $[\text{Ag}(\text{4,4',4'',4'''-tetracyanotetraphenylmethane})\text{CF}_3\text{SO}_3] \cdot 3\text{C}_6\text{H}_6$. This structure results from the capping of a coordination site of silver(I) by the triflate counterion. (b, bottom) An ORTEP (35% thermal ellipsoids) showing the coordination geometry of silver(I) in $[\text{Ag}(\text{4,4',4'',4'''-tetracyanotetraphenylmethane})\text{CF}_3\text{SO}_3] \cdot 3\text{C}_6\text{H}_6$. Silver(I) coordinates to three nitriles of the organic ligand and a triflate counterion.

structure of $[\text{Ag}(\text{1,3,5-triazine})(\text{CF}_3\text{SO}_3)] \cdot \text{H}_2\text{O}$ (**8**) is characterized by a three-dimensional, (10,3) net. The structures of $[\text{Ag}(\text{1,3,5-tricyanobenzene})(\text{CF}_3\text{SO}_3)]$ (**9**)

and $[\text{Ag}(\text{1,3,5-tris(4-ethynylbenzonitrile)benzene})\text{CF}_3\text{SO}_3] \cdot 2\text{C}_6\text{H}_6$ (**12**) can be considered as homeotypic with a common 3-connected prototype, AlB_2 , while the

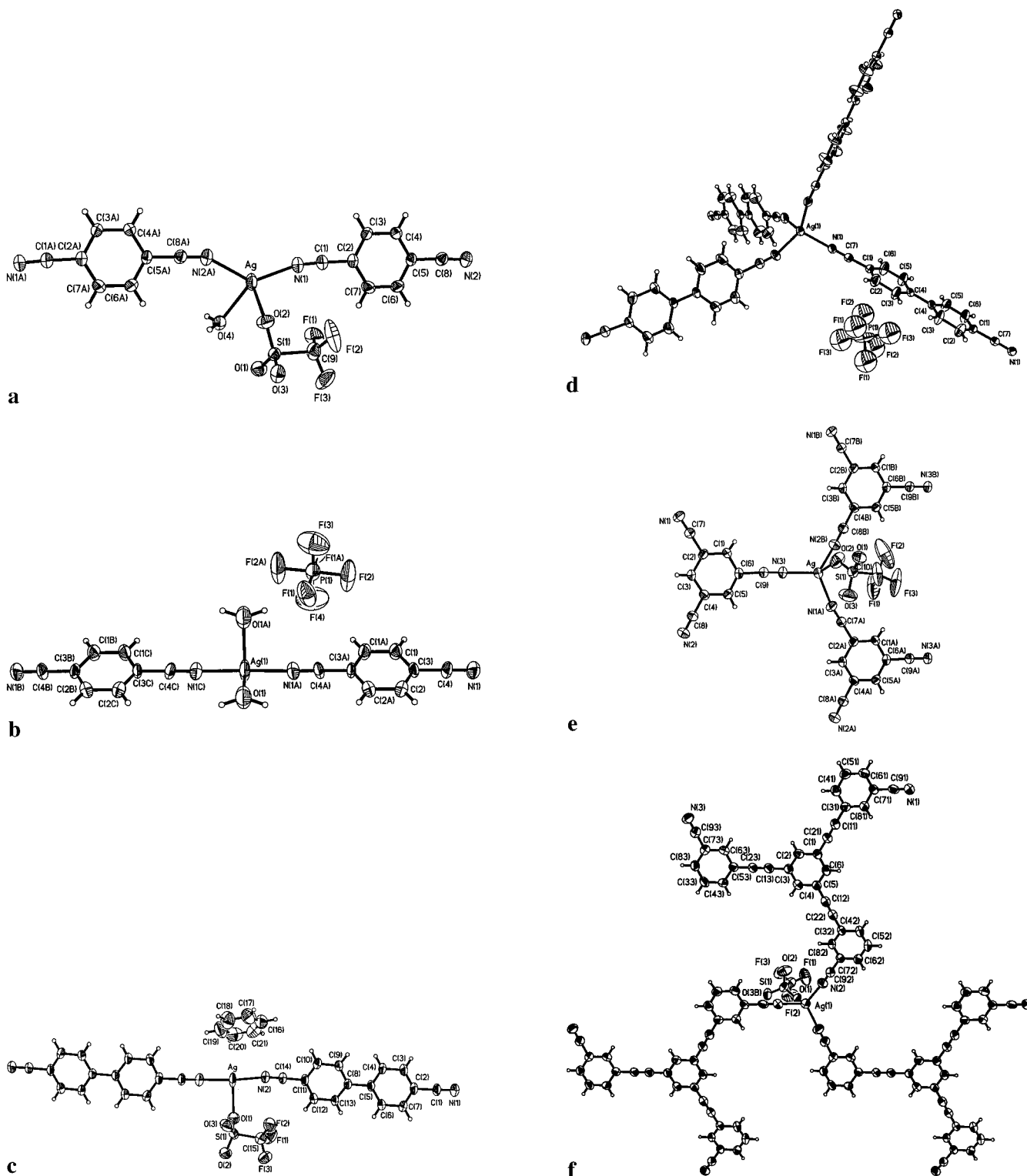


Figure 6. Illustration of coordination spheres of silver(I) in the complexes of multitopic ligands with silver(I) salts. (a) ORTEP (50% probability ellipsoids) showing the coordination sphere of silver(I) in the $[\text{Ag}(\text{1,4-dicyanobenzene})(\text{CF}_3\text{SO}_3)(\text{H}_2\text{O})_{0.5}]$ complex. Silver(I) adopts a trigonal-pyramidal geometry with two nitrogen atoms and the oxygen of triflate in the basal plane and the oxygen of water in the axial position. (b) Coordination sphere of silver(I) in the structure of $[\text{Ag}(\text{1,4-dicyanobenzene})(\text{H}_2\text{O})]\text{PF}_6$. Silver(I) adopts a sawhorse geometry with the two nitrogen atoms of the ditopic ligand and two oxygen atoms of the water molecules in the coordination sphere. (c) ORTEP (50% probability ellipsoids) showing the coordination sphere of silver(I) in the structure of $[\text{Ag}(\text{4,4'-biphenyldicarbonitrile})\text{CF}_3\text{SO}_3] \cdot \text{C}_6\text{H}_6$. Silver(I) adopts a T-shaped geometry with the two nitrogen atoms of the ditopic ligand and an oxygen atom of triflate in the coordination sphere. A weak $\text{Ag}(\text{I})$ –benzene interaction at a Ag –ring plane distance of 3.28 Å is observed. The triflate counterion was modeled as being disordered over three sites. The major occupancy site is shown here. (d) ORTEP (50% probability ellipsoids) showing the coordination sphere of silver(I) in the structure of $[\text{Ag}(\text{4,4'-biphenyldicarbonitrile})_2]\text{PF}_6$ (A). Silver(I) adopts a tetrahedral geometry with the four nitrogen atoms of the ditopic ligand. (e) ORTEP (35% probability ellipsoids) showing the coordination sphere of silver(I) in the structure of $[\text{Ag}(\text{1,3,5-tricyanobenzene})(\text{CF}_3\text{SO}_3)]$. Silver(I) adopts a trigonal-pyramidal geometry with three nitrogen atoms in the basal plane and an oxygen of triflate in the axial position. (f) Illustration of the trigonal-pyramidal coordination environment around silver(I) in the X-ray crystal structure of $[\text{Ag}(\text{1,3,5-tris(3-ethynylbenzonitrile)benzene})\text{CF}_3\text{SO}_3] \cdot 2\text{C}_6\text{H}_6$.

complex $[\text{Ag}(1,3,5\text{-tris(4-ethynylbenzonitrile)benzene})\text{CF}_3\text{SO}_3] \cdot 2\text{C}_6\text{H}_6$ (A) (**11**)^{6d} is a structural analogue of ThSi_2 . [12]Annulene-like units constitute the structure of $[\text{Ag}(1,3,5\text{-tris(3-ethynylbenzonitrile)benzene})\text{CF}_3\text{SO}_3] \cdot 2\text{C}_6\text{H}_6$ (**13**).^{7c}

The tetratopic ligand 4,4',4'',4'''-tetracyanotetraphenylmethane is known to form diamondoid nets with Cu(I).³⁰ If the triflate counterion coordinates to silver(I), the ML stoichiometry required for the formation of a diamondoid net is not possible. The inability of silver(I) to extend its coordination number beyond four would, therefore, result in at most a 3-connected network. Indeed, this tetratopic ligand yielded an undulating, graphitic sheet leaving one of the four nitriles of the tetratopic ligand uncoordinated (see Figure 5a). The other possible networks that did not form but are reasonable are the (4,3)-connected net and the (4,2)-connected net (comprised of a large adamantanoid unit). While the former net is rare even among inorganic solid-state structures,³¹ the latter will not result in closest packing.

In contrast to the triflate complexes discussed here, the networks that result from the complexation of ditopic ligands with silver(I) salts of noncoordinating counterions such as BF_4^- , PF_6^- , and SbF_6^- are quite varied. While one-dimensional, infinite chains constitute the complexes of pyrazine and 1,4-dicyanobenzene with silver(I) hexafluorophosphate, three-dimensional, 9-fold interpenetrated diamondoid nets characterize the silver(I) hexafluorophosphate complex of 4,4'-biphenyldicarbonitrile.^{7d} Recently, Ciani et al. have shown that a variety of networks result from the complexes of pyrazine with AgBF_4 , AgPF_6 , and AgSbF_6 .^{2c,d}

In conclusion, we have shown that metal coordination in the solid state may be influenced by the use of a coordinating counterion in conjunction with the topicity of the ligand. For the silver(I) complexes presented here employing the weakly coordinating triflate counterion,

ditopic ligands form one-dimensional, chainlike structures, while tritopic ligands form 3-connected nets. The tetratopic ligand used also forms 3-connected nets due to the capped silver(I) coordination. As more examples become available, it will be of interest to see if these trends continue to hold. Although many factors must be considered in attempting to predict network packing, we feel that through the structures presented, Ag–N interactions, like hydrogen bonding, can be reliably used for the construction of networks by the supramolecular chemist.

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Supporting Information Available: Crystallization protocol employed for the structural study, tables of structure summary, atomic coordinates, thermal parameters, and bond lengths and angles for the complexes $[\text{Ag}(1,4\text{-pyrazine})_{1.5}\text{CF}_3\text{SO}_3]$, $[\text{Ag}(1,4\text{-pyrazine})](\text{PF}_6)_{0.5}(\text{OH})_{0.5}$, $[\text{Ag}(1,3,5\text{-triazine})(\text{CF}_3\text{SO}_3)] \cdot \text{H}_2\text{O}$, $[\text{Ag}(1,3,5\text{-tris(4-ethynylbenzonitrile)benzene})\text{CF}_3\text{SO}_3] \cdot 2\text{C}_6\text{H}_6$ polymorph (B) and $[\text{Ag}(4,4',4'',4'''\text{-tetracyanotetraphenylmethane})\text{CF}_3\text{SO}_3] \cdot 3\text{C}_6\text{H}_6$ (27 pages); observed and calculated structure factors (75 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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