Inorg. Chem. **2004**, *43*, 4953–4961

Inorganic Chemistry
Article

Coordination Networks through the Dimensions: From Discrete Clusters to 1D, 2D, and 3D Silver(I) Coordination Polymers with Rigid Aliphatic Amino Ligands

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Received February 17, 2004

The use of a ligand directed strategy in the assembly of discrete clusters, 1D chains, 2D layers, and 3D networks using aliphatic N-donor ligands has been investigated. The ligands are a family of amines with rigid backbones [*cis,cis*-1,3,5-triaminocyclohexane (*cis*-tach), *cis,trans*-1,3,5-triaminocyclohexane (*trans*-tach), *cis*-1,3-diaminocyclohexane (*cis*-dach), and *cis*-3,5-diaminopiperidine (*cis*-dapi)], and their complexation with Ag(I) salts results in a diverse set of architectures with the following compositions: $[Ag_3(cis\text{-tach})_2]F_3 \cdot 4CH_3OH \cdot 0.5H_2O$ (**1**), $[Ag_3(cis\text{-tach})_2]F_3 \cdot 6H_2O$ (**2**), $\{[Ag(cis\text{-dach})]ClO_4\}_n$ (**3**), $\{[Ag(cis\text{-tach})]NO_3\}_n$ (**4**), $\{[Ag(trans\text{-tach})]PF_6\}_n$ (**5**), and $\{[Ag(cis\text{-dapi})]CF_3SO_3\}_n$ (**6**). Structural analysis shows that compounds **1** and **2** are discrete M_3L_2 cage-type clusters with varying solvent molecule content. Short Ag···Ag contacts (3.021(8) Å) are observed to dimerize discrete units in compound **2**. Compound **3** is a 1D zigzag chain formed by coordination to the two primary amines of *cis*-dach, whereas the tridentate ligands in compounds **4** and **5** (*cis*-tach and *trans*-tach, respectively) are able to form tubular architectures by virtue of their ability to “wrap” round the channel walls. An infinite 2D coordination network is demonstrated by compound **6**, in which the three coplanar amino donors of *cis*-dapi coordinate to the trigonal planar Ag(I) ions to form a layered structure of 6^3 topology. These are compared with a previously reported 3D structure, $\{[Ag(trans\text{-tach})]NO_3\}_n$ (**7**), that belongs to this family of architectures.

Introduction

Much interest currently lies in the field of self-assembled coordination polymers due to potential application as new functional solid materials as well as expanding the understanding of the assembly processes that underpin the formation of clusters and multidimensional networks.[1] This has stimulated a great deal of attention towards the design and construction of polynuclear coordination networks to perform highly specific and cooperative functions.[2] By using well defined metal and ligand building blocks it is possible to predictably assemble many intricate architectures, including two-dimensional polygons and three-dimensional architectures.[3] Silver(I) in particular has been used to construct a great number of geometrically and stereochemically interesting 1D,[4] 2D,[5] and 3D[6] infinite networks with coordination numbers ranging between two and six. To date, a great deal of emphasis has been placed on the self-assembly of silver(I) coordination polymers using multitopic rigid ligands that possess a considerable degree of preorganization. Many

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10.1021/ic049786i CCC: $27.50

polypyridyl-based ligands such as 4,4′-bipyridyl[7] and a more limited number of highly rigid aliphatic amino ligands such as hexamethlyenetetramine[8] have led to the self-assembly of low-dimensionality networks such as one-dimensional systems and tubular frameworks[9] as well as high-dimensionality polymers with functional properties.[10]

In this study we report our investigations into the coordination chemistry of a family of rigid, aliphatic di- and triamino ligands with a range of silver(I) salts (F^-, ClO_4^-, NO_3^-, PF_6^-, and $CF_3SO_3^-$). This study aims to further the understanding of how the resulting coordination networks can be manipulated by both engineering degrees of geometric freedom into the ligand system and by utilizing different counteranions. In this respect, the four ligands *cis*,*cis*-1,3,5-triaminocyclohexane (*cis*-tach), *cis*,*trans*-1,3,5-triaminocyclohexane (*trans*-tach), *cis*-1,3-diaminocyclohexane (*cis*-dach), and *cis*-3,5-diaminopiperidine (*cis*-dapi) are members of a family of sterically constrained cyclic polyamines. The rigidity of the six-membered backbone restricts the geometric freedom of the coordinating nitrogen atoms. However, the nonplanarity of the ligands and the presence of the primary aliphatic amino groups facilitate a great deal more torsional flexibility compared to previously reported rigid ligands.[4,5] This study also expands and unites our previous investigations into silver(I) coordination networks with aliphatic amino ligands.[11,12] Thus we present six new architectures, assembled using rigid aliphatic amino ligands, that span diverse architectures from discrete molecules ([Ag_3(*cis*-tach)$_2$]F_3.4CH_3OH·0.5H_2O (**1**) and [Ag_3(*cis*-tach)$_2$]F_3·6H_2O (**2**)) to one- ([Ag(*cis*-dach)]ClO_4 (**3**), [Ag(*cis*-tach)]NO_3 (**4**), and [Ag(*trans*-tach)]PF_6 (**5**)) and two-dimensional coordination polymers ([Ag(*cis*-dapi)]CF_3SO_3 (**6**))—as well as the contextual analysis of a previously reported three-dimensional coordination network, [Ag(*trans*-tach)]NO_3 (**7**).[11]

Experimental Section

Materials and Methods. Ligands *cis*,*cis*- and *cis*,*trans*-1,3,5-triaminocyclohexane,[13] *cis*-1,3-diaminocyclohexane,[14] and *cis*-1,3-diaminopiperidine[15] were synthesized according to literature procedures. All other solvents and reagents were used as bought without further purification. NMR spectra were measured in D_2O on a Bruker DPX-400 (400 MHz 1H). Infrared spectra were obtained from samples prepared as KBr disks in the 650−4000 cm^{-1} range using a Jasco FTIR-410 spectrometer. Elemental analyses were performed on a CE-440 Elemental Analyzer.

Preparation of [$Ag_3(C_6H_{15}N_3)_2$]F_3·4CH_3OH·0.5H_2O (1). Silver fluoride (64 mg, 0.51 mmol) in methanol (2 mL) was added dropwise to a methanolic solution of *cis,cis*-1,3,5-triaminocyclohexane (65 mg, 0.51 mmol) and stirred at room temperature for 1 h. The clear, colorless solution was filtered and yielded small platelike, colorless crystals suitable for diffraction by diffusion with diethyl ether. Yield 26 mg (0.034 mmol, 6.56%). [$Ag_3(C_6H_{15}N_3)_2$]F_3·4CH_3OH·0.5H_2O (776.21); found (calc.)%: C 24.93 (24.76), H 6.22 (6.10), N 10.54 (10.83); ^{1}H NMR (D_2O, ppm) 0.96 (pq, 3H, J 11.46 Hz), 2.22 (dt, 3H, J 3.91, 11.41 Hz), 3.24 (m, 3H); FTIR (KBr, cm^{-1}) 3329 (m), 3276 (m), 1583 (m), 1456 (m), 1384 (m), 1267 (s), 1231 (s), 1175 (s), 1029 (s), 950 (m), 927 (m), 815 (w), 759 (w).

Preparation of [$Ag_3(C_6H_{15}N_3)_2$]F_3·6H_2O (2). Silver fluoride (25 mg, 0.19 mmol) in methanol (2 mL) was added dropwise to a methanolic solution of *cis,cis*-1,3,5-triaminocyclohexane (50 mg, 0.39 mmol) and stirred at room temperature for 1 h. The resulting light suspension was filtered, and the clear, colorless solution yielded small platelike, colorless crystals suitable for diffraction by diffusion with diethyl ether. Yield 80 mg (0.11 mmol, 56%). [$Ag_3(C_6H_{15}N_3)_2$]F_3·6H_2O (747.13); found (calc.)%: C 19.32 (19.29), H 5.34 (5.66), N 11.60 (11.24); ^{1}H NMR (D_2O, ppm) 0.97 (pq, 3H, J 11.50 Hz), 2.22 (dt, 3H, J 3.90, 11.36 Hz), 3.26 (m, 3H); FTIR (KBr, cm^{-1}) 3329 (m), 3282 (m), 1583 (m), 1456 (m), 1384 (m), 1268 (s), 1228 (s), 1175 (s), 1027 (s), 950 (m), 925 (m), 814 (w), 759 (w).

Preparation of [$Ag(C_6H_{14}N_2)$]ClO_4 (3). Silver(I) perchlorate (55 mg, 0.26 mmol) in methanol (4 mL) was added dropwise to a solution of *cis*-1,3-diaminocyclohexane (60 mg, 0.52 mmol) in methanol (4 mL). Upon stirring a white precipitate occurs, which dissolved partially after addition of water (3 mL) to give a very fine white precipitate. Filtration removed all solid to yield a clear, colorless solution that yielded crystals suitable for diffraction by diffusion of diethyl ether. Yield 28 mg (0.08 mmol, 33%). [$Ag(C_6H_{14}N_2)$]ClO_4 (321.51); found (calc.)%: C 21.98 (22.41), H 4.26 (4.38), N 8.51 (8.31); ^{1}H NMR (D_2O, ppm) 0.87 (m, 3H), 1.22 (m, 1H), 1.70 (m, 1H), 1.79 (m, 2H), 1.96 (dhep, 1H, J 2.1, 11.67 Hz), 2.62 (tt, 2H, J 3.79, 11.11 Hz); FTIR (KBr, cm^{-1}) 2925 (w), 2854 (w), 2098 (m), 1596 (m), 1452 (s), 1357 (m), 1176 (w).

Preparation of [$Ag(C_6H_{15}N_3)$]NO_3 (4). Silver nitrate (43 mg, 0.25 mmol) in methanol (3 mL) was added dropwise to a methanolic solution of *cis,cis*-1,3,5-triaminocyclohexane (65 mg, 0.51 mmol) and stirred at room temperature for 30 min, during which a white solid precipitated. Water (6 mL) was added, and the mixture was stirred at room temperature for a further 30 min. The resulting clear colorless solution was filtered and yielded colorless block crystals suitable for diffraction by slow evaporation of mother liquor over 7 months. Yield: 38 mg (0.11 mmol, 51%). [$Ag(C_6H_{15}N_3)$]NO_3 (299.09); found (calc.)%: C 24.69 (24.09), H 5.44 (5.055), N 18.73 (18.73); ^{1}H NMR (D_2O, ppm) 0.97 (q, 3H, J 11.60 Hz), 2.02 (m, 3H), 2.92 (tt, 3H, J 3.72, 11.84 Hz); FTIR (KBr, cm^{-1}) 3340 (m), 3291 (m), 3241 (m), 3160 (w), 2915 (m), 2852 (w), 1585 (m), 1457 (w), 1376 (s), 1307 (s), 1199 (m), 1130 (m), 1078 (m), 1064 (m), 1041 (s), 946 (m), 917 (m), 898 (m), 865 (w), 854 (w), 823 (m).

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Table 1. Crystallographic Data for **1**−**6**[a]

	1	**2**	**3**	**4**	**5**	**6**
empirical formula	$C_{16}H_{47}Ag_3F_3N_6O_{4.5}$	$C_{12}H_{43}Ag_3F_3N_6O_6$	$C_6H_{14}AgClN_2O_4$	$C_6H_{15}AgN_4O_3$	$C_6H_{15}AgF_6N_3P$	$C_6H_{13}AgF_3N_3O_3S$
fw	776.21	747.13	321.51	299.09	382.05	372.12
cryst system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	orthorhombic
a (Å)	15.6080(4)	8.0479(5)	6.3452(8)	8.2530(3)	6.7103(3)	11.5983(4)
b (Å)	8.0156(2)	22.5030(13)	9.8756(15)	7.7035(3)	9.2963(4)	12.1522(4)
c (Å)	22.5902(6)	14.0842(9)	8.4770(12)	15.8134(4)	9.9428(3)	16.3011(5)
α (deg)	90	90	90	90	104.974(2)	90
β (deg)	104.514(2)	100.999(3)	106.703(8)	104.786(2)	100.175(3)	90
γ (deg)	90	90	90	90	98.015(2)	90
space group	$P2_1/c$	$P2_1/c$	$P2_1/m$	$P2_1/n$	P-1	$Pbca$
V (Å^3)	2736.001(12)	2503.8(3)	508.78(12)	972.08(6)	578.48(4)	2297.56(13)
Z value	4	4	2	4	2	8
ρ_{calcd} (g/cm^3)	1.884	2.006	2.099	2.044	2.193	2.152
μ (cm^{-1})	2.180	0.2385	0.2235	0.2063	0.1942	0.1978
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
no. observations	5361	4129	1063	12126	11790	2628
residuals: R; wR	0.0518; 0.1279	0.0662; 0.1328	0.0352; 0.0667	0.0161; 0.0368	0.0223; 0.0515	0.0461; 0.0695

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$.

Preparation of $[Ag(C_6H_{15}N_3)]PF_6$ (5). Silver(I) hexafluorophosphate (64 mg, 0.26 mmol) in methanol (4 mL) was added dropwise to a solution of *cis*,*trans*-1,3,5-triaminocyclohexane (65 mg, 0.51 mmol) in methanol (4 mL). The resulting white precipitate dissolved completely after addition of water (2 mL) to give a clear, colorless solution. Single crystals suitable for diffraction were grown by diffusion of diethyl ether. Yield 65 mg (0.17 mmol, 65%). $[Ag(C_6H_{15}N_3)]PF_6$ (382.05); found (calc.)%: C 19.01 (18.89), H 3.97 (3.96), N 11.11 (11.03); ^{1}H NMR (D_2O, ppm) 1.08 (q, 1H, J11.71 Hz), 1.31 (td, 2H, J1.97, 12.13 Hz), 1.88 (d, 2H, J12.54 Hz), 2.26 (m, 1H), 3.19 (t, 2H, J11.79), 3.39 (t, 1H, J12.14 Hz); FTIR (KBr, cm^{-1}) 3249 (m), 3099 (w), 2883 (w), 2360 (m), 1646 (m), 1610 (s), 1556 (s), 1477 (m), 1455 (m), 1436 (s), 1378 (s), 1336 (s), 1311 (m), 1286 (m), 1184 (m), 1112 (m), 1087 (m), 1041 (m), 1004 (m), 946 (m), 887 (w), 827 (s), 759 (w).

Preparation of $[Ag(C_5H_{13}N_3)]CF_3SO_3$ (6). Silver triflate (112 mg, 0.43 mmol) in methanol (5 mL) was added dropwise to a methanolic solution of *cis*-3,5-diaminopiperidine (100 mg, 0.87 mmol) and stirred at room temperature for 30 min. The reaction mixture was concentrated to 2 mL, and the clear yellow solution yielded crystals suitable for diffraction by diffusion of diethyl ether. Yield 146 mg (0.57 mmol, 66%). $[Ag(C_5N_3H_{13})]CF_3SO_3$ (372.12); found (calc.)%: C 19.99 (19.37), H 3.51 (3.52), N 11.49 (11.29); ^{1}H NMR (D_2O, ppm) 1.08 (pq, 1H), 2.13 (pt, 2H), 2.22 (m, 1H), 2.89 (m, 2H), 3.05 (m, 2H); FTIR (KBr, cm^{-1}) 3430 (bs), 3321(s), 2918 (m), 2810 (w), 1603 (s), 1452 (w), 1383 (w), 1257 (vs), 1169 (s), 1099 (m), 1028 (s), 924 (m), 850 (w), 760 (w), 640 (s), 573 (m), 515 (m).

Single-Crystal Structure Determination. Suitable single crystals of **1**−**6** were grown and mounted onto the end of a thin glass fiber using Fomblin oil. X-ray diffraction intensity data were measured at 150 K on a Nonius Kappa-CCD diffractometer [λ(Mo−Kα) = 0.7107 Å]. Structure solution and refinement for **1**−**6** was carried out with SHELXS-97[16] and SHELXL-97[17] via WinGX.[18] Corrections for incident and diffracted beam absorption effects were applied using empirical[19] or numerical methods.[20] Compounds **1** and **2** crystallized in the space group $P2_1/c$, compound **3** in $P2_1/n$, compound **4** in $P2_1/m$, compound **5** in P-1, and compound **6** in $Pbca$, as determined by systematic absences in the intensity data, intensity statistics, and the successful solution and refinement of the structures. All structures were solved by a combination of direct methods and difference Fourier syntheses and refined against F^2 by the full-matrix least-squares technique. Crystal data, data collection parameters, and refinement statistics for **1**−**6** are listed in Table 1. Relevant interatomic bond distances and bond angles for **1**−**6** are given in Table 2.

Results and Discussion

Ligand Design. The ligands designed for this investigation are related as aliphatic amines based around a rigid six-membered backbone containing a *cis*-1,3-diamino moiety. Contrary to many of the ligands reported,[4,5] these molecules are preorganized and possess an additional degree of flexibility in the coordination geometry of the amino groups (Figure 1). The energetically favorable conformer, in which the two core amino groups are in *cis*-equatorial positions on the cyclohexane ring, is maintained in compounds **1**−**7** as every amino group of each ligand coordinates to a different silver(I) ion. The bidentate ligand *cis*-dach[21] represents the core of each ligand. The rigidity of the cyclohexane backbone ensures that the *cis*-1,3-diamino groups are held in the equatorial position. The coordinating amines therefore form a bidentate, planar geometry. *cis*-Dapi[15] has, in addition to the core diamino binding mode, a third coordinating amino group. The μ-3 donor set is completed by a secondary amine located within the six-membered backbone. The secondary amino group has limited coordination flexibility as compared to the primary amino groups and therefore constructs a tridentate coordination plane coplanar to the rigid backbone. *cis*-Tach[22] is a μ-3 ligand with the third, in this case primary, amino group extended away from the cyclohexane ring. This confers a significant amount of flexibility as the torsion angle

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Table 2. Bond Lengths (Å) and Angles (deg) for **1**−**6**

compound	bond distances				bond angles	
1	Ag(1)−N(1)	2.136(5)	Ag(1)−N(4)	2.142(5)	N(1)−Ag(1)−N(4)	172.5(2)
	Ag(2)−N(2)	2.115(5)	Ag(2)−N(5)	2.127(5)	N(2)−Ag(2)−N(5)	174.4(2)
					N(3)−Ag(3)−N(6)	171.9(2)
2	Ag(1)−Ag(#1)	3.020(19)	Ag(1)−N(1)	2.144(8)	N(1)−Ag(1)−N(4)	172.9(3)
	Ag(1)−N(4)	2.108(9)	Ag(2)−N(2)	2.123(9)	N(2)−Ag(2)−N(5)	171.7(4)
	Ag(2)−N(5)	2.148(9)	Ag(3)−N(3)	2.139(9)	N(3)−Ag(3)−N(6)	171.5(4)
	Ag(3)−N(6)	2.141(9)				
3	Ag−N	2.151(3)			N−Ag−N	180.0(3)
4	Ag−N(1)	2.166(16)	Ag−N(2)	2.161(16)	N(1)−Ag−N(2)	151.77(6)
	Ag−N(3)	2.408(16)			N(1)−Ag−N(3)	107.60(6)
					N(2)−Ag−N(3)	100.31(6)
5	Ag−N(1)	2.261(2)	Ag−N(2)	2.368(2)	N(1)−Ag−N(2)	118.09(8)
	Ag−N(3)	2.299(2)			N(1)−Ag−N(3)	141.10(8)
					N(2)−Ag−N(3)	100.77(8)
6	Ag−N(1)	2.390(4)	Ag−N(2)	2.244(4)	N(1)−Ag−N(2)	105.77(13)
	Ag−N(3)	2.236(4)			N(1)−Ag−N(3)	113.06(14)
					N(2)−Ag−N(3)	140.95(15)

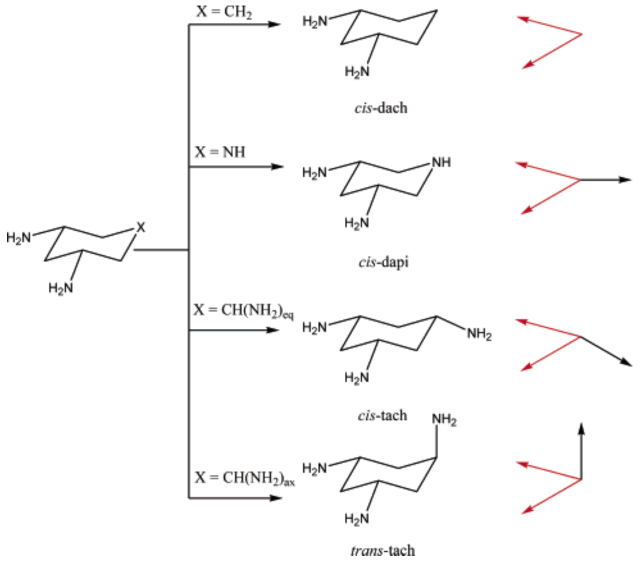

Figure 1. The design strategy to create a range of binding geometries using aliphatic amines.

along the C−N bonds can be distorted upon coordination. This third amino group is *cis* to the core binding mode, creating a tripodal C_3 ligand with three equal C−N vectors available for coordination. *trans*-Tach[11,23] is the isomeric conformer of *cis*-tach, where the third amino group is *trans* to the core binding mode. This axial group provides an extra vector and therefore has the potential for higher dimensionality coordination.

Structural Analysis of [Ag_3(*cis*-tach)$_2$]F_3·4CH_3OH·0.5H_2O (1) and [Ag_3(*cis*-tach)$_2$]F_3·6H_2O (2). Crystallization of a mixture of *cis*-tach and AgF by diffusion with ether yields a discrete, cage-type coordination compound with the composition M_3L_2 (Figure 2a). Differences in the solvent molecules included in the crystal lattice result in the formation of the same M_3L_2 cage structure but with short Ag···Ag contacts in compound **2** (Figure 2b). In both structures all three *cis*-equatorial amino groups of the *cis*-tach ligands are involved in coordinative interactions to Ag(I) ions. The asymmetric unit of **1** consists of two *cis*-tach ligands and three crystallographically independent Ag(I) ions [Ag(1), (2), and (3)] as well as three fluoride counterions, four methanol solvent molecules, and half a water molecule. The asymmetric unit of **2** consists of two *cis*-tach ligands and three crystallographically independent Ag(I) ions [Ag(1), (2), and (3)] as well as three fluoride counterions and six molecules. Each cylindrical cage structure is formed by three Ag(I) ions connecting two capping *cis*-tach molecules in eclipsed conformation when viewed along the N−Ag−N vector. Twelve-membered macrocycles form each of the three faces of the cage and the linear coordination of Ag(2) in **1** and Ag(1) in **2** is distorted slightly toward the neighboring unit. The two closest Ag(2) atoms in **1** are separated by 4.389 Å and hence do not interact. However, the two closest Ag(1) ions in **2** are positioned to give a short intermolecular Ag···Ag contact (3.021(18) Å). This contact occurs exclusively between Ag(1)···Ag(#1) ions, thus no polymeric species is formed. This has been investigated by preliminary DFT calculations which do indicate significant overlap and bonding interactions. Furthermore a survey of short Ag···Ag interactions in the CSD database demonstrates that the observed distance is exactly as expected.[24] Although generally longer than ligand-supported metal pairs, direct metal−metal contacts have been reported for Ag(I)···Ag(I)[24] and are more common for the metallophilic Au(I) ion.[25]

It appears that the intricate hydrogen bonding present in **1** and **2** has a significant impact on the resulting coordination compounds. The structure of compound **1** contains both methanol solvent molecules and water molecules, both of which are involved in hydrogen-bonded interactions with the coordinating amino groups. The noninteracting methyl groups of the disordered methanol molecules form “pockets” within the packed array. Furthermore, the coordination complexes present in compound **1** are packed around these pockets, forming hydrogen-bonded interactions with the fluoride counterions (N−H···F between 2.759(7) and 2.996(7) Å) and

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(23) (a) Seeber, G.; Kariuki, B. M.; Cronin, L. *Chem. Commun.* **2002**, 2912. (b) Seeber, G.; Long, D.-L.; Kariuki, B. M.; Cronin, L. *J. Chem. Soc., Dalton Trans.* **2003**, 4498.

(24) (a) A survey of Ag(I)···Ag(I) interactions between 2 and 5 Å in CSD gave a median of 3.00 Å from 423 observations. (b) Density functional theory calculations (including Löwdin and Mulliken population analysis) using the TURBOMOLE package (Treutler. O.; Ahlrichs. R, *J. Chem. Phys.* **1995**, *102*, 346) employed TZVP basis sets and the Becke-Perdew (BP86) exchange-correlation functional. (c)Villanneau, R.; Proust, A.; Robert, F.; Gouzerh, P. *Chem. Commun.* **1998**, 1491.

(25) Schmidbaur, H. *Gold Bull.* **1990**, *23*, 11.

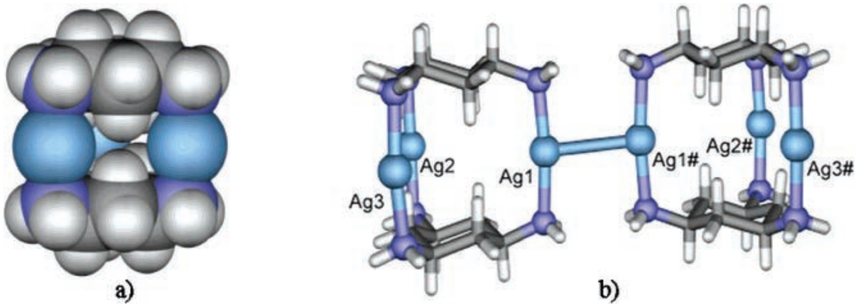

Figure 2. (a) Space-filling representation of the units in **1**. (b) Linked units of **2** showing short Ag···Ag contacts. Hydrogen atoms are shown as white sticks and carbon atoms as gray sticks, and Ag(I) ions are represented by large light blue spheres and nitrogen atoms by small dark blue spheres.

the oxygen atoms from the methanol and water molecules (N−H···O between 2.944(7) and 2.996(7) Å). Crucially, the absence of methanol solvent molecules in the structure of compound **2** appears to have a marked effect on the resulting array. Here, two cage units are aligned such that hydrogen-bonded interactions between the amino group from each cage and a bridging fluoride counterion (N(1)−H(1A)···F(1) 2.952(11) Å; N(4)−H(4A)···F(1) 2.890(12) Å) are formed. Therefore, circumstantially, the formation of these (cage1)-N···F···N(cage2) hydrogen bonds appears to be linked with the formation of the short silver(I)−silver(I) contacts. Further, the dimeric connected units are packed in ABAB fashion perpendicular to the crystallographic *a* axis, with hydrogen bonded interactions between the coordinating amino groups and the fluoride counterions (N−H···F between 2.886(11) and 2.968(12) Å) and the oxygen atoms of the water molecules (N−H···O between 2.839(13) and 3.162(14) Å). See Supporting Information a for full details and figures showing the hydrogen-bonded networks in **1** and **2**.

One pertinent aim should be to extend these systems so that the cavity size allows the encapsulation of molecules. Such cavity containing structures could be extremely promising in a wide-variety of applications such as host−guest chemistry[26] and catalysis.[27] Specifically, two examples of M_3L_2 coordination compounds can be found in the literature. The first M_3L_2 compound to be characterized by single-crystal X-ray crystallography is constructed from two capping tripodal ligands and three tetrahedral zinc(II) centers, forming a large, almost spherical cavity (ligand to ligand distance is 9.49 Å).[28] The second M_3L_2 structure resembles compounds **1** and **2** in the formation a cylindrical cage (ligand to ligand distance is 10.99 Å).[29] However, space-filling representations show that the voids in compounds **1** and **2** are not of sufficient dimensions to sustain encapsulation of solvent molecules or even the small fluoride counterions (ligand-to-ligand distances are 5.331 and 4.896 Å, respectively).

Structural Analysis of [Ag(*cis*-dach)]ClO$_4$ (3). Crystallization of a methanolic mixture of *cis*-dach with AgClO$_4$ by evaporation over 2 weeks yields a polymeric chain with a metal-to-ligand ratio of 1:1. Both equatorial amino groups of *cis*-dach are involved in coordinative interactions to Ag(I) ions. The asymmetric unit consists of one *cis*-dach ligand and one Ag(I) ion as well as one perchlorate counterion. No solvent molecules are present in the crystal lattice. The polymer is formed by linear Ag(I) ions coordinating to two primary amino groups of two independent *cis*-dach ligands (Figure 3). The zig−zig chains are aligned one above the other (interchain distances are 6.345 and 8.477 Å) and are held together in a three-dimensional hydrogen-bonded network by interactions between the coordinating amino groups and the perchlorate counterions (N−H···O between 3.251(4) and 3.259(4) Å) and to a weaker extent between the methylene protons C(1)−H(1) and the perchlorate counterions (C−H···O are between 3.377(6) and 3.491(7) Å).

Structural Analysis of [Ag(*cis*-tach)]NO$_3$ (4). Crystallization of an aqueous methanolic solution of *cis*-tach and AgNO$_3$ by slow evaporation over a period of several months yields a one-dimensional coordination polymer with a metal-to-ligand ratio of 1:1. All three *cis*-equatorial amino groups of *cis*-tach are involved in coordinative interactions to Ag(I) ions. The asymmetric unit consists of one *cis*-tach ligand and one Ag(I) ion as well as one nitrate counterion. No solvent molecules are present in the crystal lattice. The $4^2{\cdot}6$ topology is formed by two silver atoms and two *cis*-tach units (both seen as three connected nodes) coordinated via all three amino groups along the polymer (Figure 4a). Each Ag(I) has a trigonal planar coordination sphere with three *cis* amines of different ligands, forming an infinite tubular channel. The Ag(I) atoms lie along the tube in two rows. The N(2) and N(3) atoms coordinate the Ag(I) atoms in one row, whereas the N(1) atoms of each ligand “wraps around” the wall of the tube to coordinate to the Ag(I) atoms of the second row. The metal coordination occurs exclusively in one dimension (perpendicular to the crystallographic *a* axis), forming isolated channels (interpolymer distances of 5.705, 8.367, and 10.164 Å). The tubes are held together in a three-dimensional hydrogen-bonded network by interactions with the nitrate counterions (N−H···O between 3.021(2) and 3.399(2) Å), which are located between the isolated one-dimensional polymers (Figure 4b). Each macrocycle, con-

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[26] (a) Parac, T. N.; Scherer, M.; Raymond, K. N. *Angew. Chem., Int. Ed.* **2000**, *39*, 1239. (b) Scherer, M.; Caulder, D. L.; Johnson, D. W.; Raymond, K. N. *Angew. Chem., Int. Ed.* **1999**, *38*, 1588. (c) Fujita, M.; Nagao, S.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 1649.

[27] (a) Ito, H.; Kusukawa, T.; Fujita, M. *Chem. Lett.* **2000**, 598. (b) Yoshizawa, M.; Takeyama, Y.; Kusukawa, T.; Fujita, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 1347.

[28] Sun, W.-Y.; Fan, J.; Okamura, T.; Xie, J.; Yu, K.-B.; Ueyama, N. *Chem. Eur. J.* **2001**, *7*, 2557.

[29] Liu, H.-K.; Sun, W.-Y.; Ma, D.-J.; Yu, K.-B.; Tang, W.-X. *Chem. Commun.* **2000**, 591.

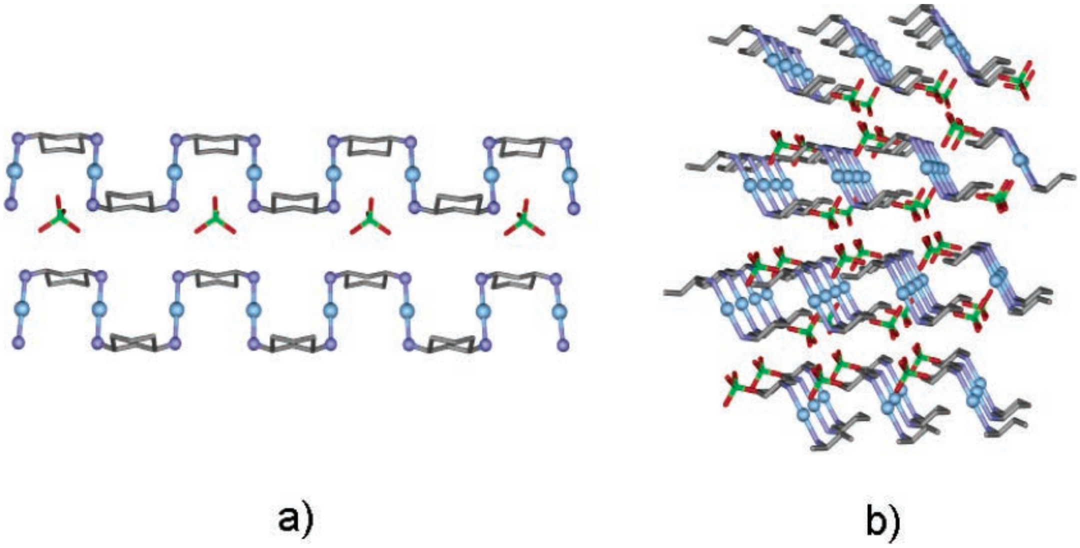

Figure 3. (a) Chain formation of **3**. (b) Packing of **3** along the crystallographic *a* axis. Hydrogen atoms are removed for clarification. Chlorine atoms are shown in green and oxygen atoms in red. Hydrogen atoms are shown as white sticks and carbon atoms as gray sticks, and Ag(I) ions are represented by large light blue spheres and nitrogen atoms by small dark blue spheres.

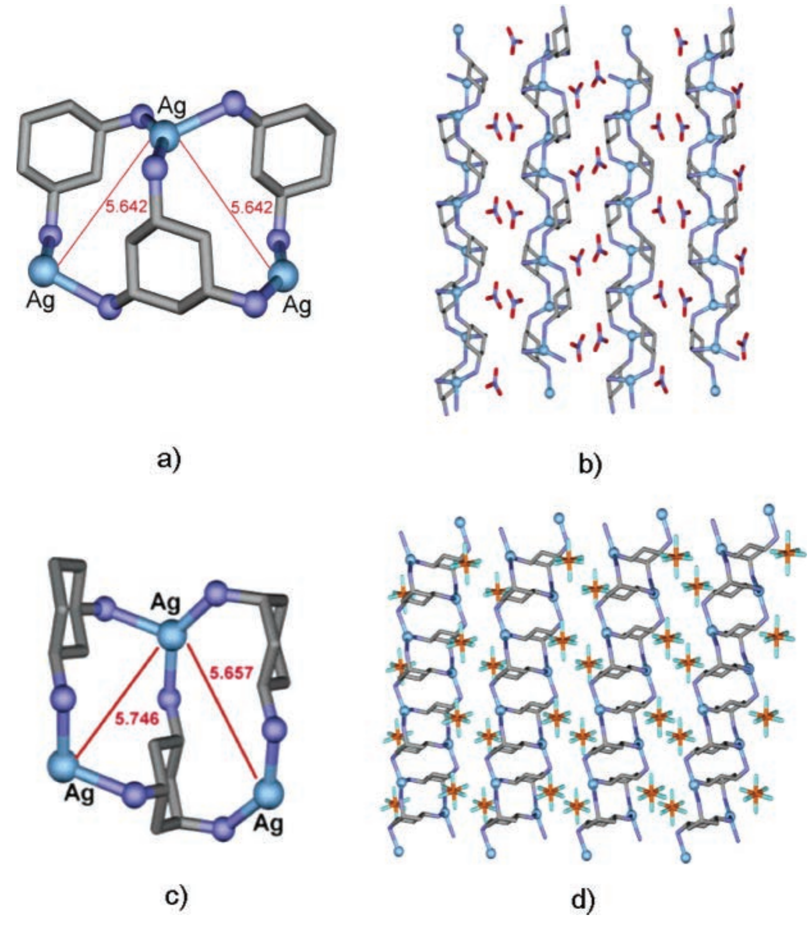

Figure 4. (a) Macrocyclic tube formation of **4**. (b) Packing of **4**. (c) Macrocyclic tube formation of **5**. (d) Packing of **5**. Hydrogen atoms are removed for clarification. Counterions: oxygen atoms are shown in red, fluorine atoms in light blue, and phosphate atoms in orange. Coordination polymer: carbon atoms are represented by gray sticks, Ag(I) ions by large light blue spheres, and nitrogen atoms by small dark blue spheres.

taining two Ag(I) ions coordinating to two amino groups of two *cis*-tach units, consists of 12 atoms with an inversion center.

Structural Analysis of [Ag(*trans*-tach)]PF$_6$ (5). Reaction of *trans*-tach with AgPF$_6$ and subsequent crystallization by diffusion of ether into the methanolic reaction mixture gives rise to isolated one-dimensional coordination polymers with a 1:1 ligand-to-metal ratio. All three amino groups of *trans*-tach are involved in coordinative interactions to Ag(I) ions. The asymmetric unit consists of one *trans*-tach ligand and one Ag(I) ion as well as one hexafluorophosphate counterion. The Ag(I) ion adopts a trigonal planar coordination sphere by coordinating to two equatorial and one axial amino group of three different *trans*-tach ligands. The overall structure is tube-like (one-dimensional coordination polymers that run perpendicular to the crystallographic *b* axis) with $4^2{\cdot}6$ topological notation, where both trigonal planar silver(I) ions and tripodal ligands are seen as three connected nodes (Figure 4c). The isolated tubes are packed in a hexagonal array, with intertubular distances of 9.296, 9.943, and 11.727 Å. Each tube is surrounded by six hexafluorophosphate counterions, which form hydrogen-bonded interactions with the amino groups of *trans*-tach (N−H···F between 3.060(3) and 3.311(3) Å), stabilizing the tubes within a three-dimensional hydrogen-bonded network (Figure 4d). The tubes are constructed by the formation of two independent 12-membered macrocycles, both with an inversion center (intermacrocyclic Ag···Ag distances are 5.657 and 5.746 Å). One macrocyclic unit is formed by the coordination of two *cis*-equatorial amino groups to two Ag(I) ions, whereas the other is formed by the coordination of the *trans*-axial and one equatorial amino group to two Ag(I) ions.

The formation of compounds **4** and **5** are further examples of synthetic routes to isolated polymeric tubes using these ligands, as the previously reported, topologically equivalent structure to **5**[12] represents a staggered chain conformation. This is formed by two chains connected through coordination of the two *cis*-equatorial amino groups to an Ag(I) ion, which are subsequently linked together via coordination of the remaining *trans*-axial amino groups to the vacant trigonal planar site of the Ag(I) ions. There are few examples of tubular coordination structures in the literature,[30,31] the most significant tubular silver(I) coordination compound having a diameter of 13.4 Å.[30] These represent, however, tubes within a higher dimensionality coordination network as coordination bonds between tubes mean that they are not truly isolated.

Structural Analysis of [Ag(*cis*-dapi)]CF_3SO_3 (6). Crystallization of a methanolic mixture of *cis*-dapi and $AgCF_3SO_3$ by diffusion with ether over 2 days gives rise to a two-dimensional coordination network with a 1:1 ligand-to-metal ratio. The asymmetric unit consists of one *cis*-dapi ligand and one silver(I) ion as well as one triflate counterion. The trigonal planar Ag(I) centers are coordinated by two primary amino groups and a secondary amino group of three *cis*-dapi ligands. The metal coordination occurs exclusively in two dimensions, forming layers of the well-known 6^3 honeycomb topological network (Figure 5). This compound is similar to a previously reported structure with this ligand,[11] which adds further evidence that the coordination geometry of the ligand can be incorporated as part of the design approach. The layers contain alternately orientated linear chains, which are held together by interchain coordination with the remaining primary amino group. Linear, intrachain coordination occurs between silver(I) atoms and the secondary ring nitrogen and a single primary amine group. The layers pack in a hexagonal array, the difference in orientation of the AB strands resulting exclusively from the orientation of the piperidine ring nitrogen along the crystallographic *b* axis. The two-dimensional coordination polymers are held together in a three-dimensional hydrogen-bonded network by interactions between the coordinating amino groups and the triflate counterions.

Summary

We have investigated the coordination behavior of a family of rigid di- and triamino ligands with a variety of Ag(I) salts to determine the way in which such ligand systems can be used in the design of new functional materials with interesting topologies. The ligands *cis,cis*-1,3,5-triaminocyclohexane, *cis,trans*-1,3,5-triaminocyclohexane, *cis*-1,3-diaminocyclohexane, and *cis*-3,5-diaminopiperidine each have coordinating aliphatic amino groups, the freedom and direction of which have significant impact on the architecture of the resulting network. The largest contributing factor, however, appears to be the choice of anion, as both *cis*- and *trans*-tach ligands are able to form coordination complexes of varying dimensionalities. This appears to depend predominantly on counterion size, as exemplified by the coordination networks formed by *trans*-tach. Here, the smaller nitrate counterion is able to sit in channels within a high dimensionality network (compound **7**), whereas the slightly larger counterions such as hexafluorophosphate appear too large to do so and rather separate the coordination polymers (compound **5**). Ligand geometry is also important in the formation of the networks—the μ_3 ligand *cis*-tach has three equatorial amino groups syn to the plane of the cyclohexane backbone, allowing the coordination as both a capping ligand to form discrete coordination compounds (compounds **1** and **2**) or a wrapping ligand in the formation of one-dimensional coordination polymers (compound **4**). The μ_3 ligand *trans*-tach, on the other hand, has two independent types of donor groups anti to the plane of the cyclohexane backbone. This enables the *trans*-axial amino group to coordinatively link two silver(I) coordination chains to form one-dimensional coordination polymers (compound **5**) and also to extend further to form three-dimensional coordination networks by the interconnection of two independent macrocyclic subunits (compound **7**,[11] Figure 6). This structure, previously reported by us, exemplifies the scope of the ligand to form high-dimensionality networks due to the presence of the additional C−N vector stemming from the rigid backbone.

Conclusions

Silver(I) coordination chemistry has, to date, focused largely on the use of planar, N-aromatic ligands. Using inherently more flexible aliphatic amino spacer units opens up a new area in the design of coordination networks, where a certain degree of flexibility can be engineered into complex formation to yield a range of networks of differing dimensionalities and topologies, see Figure 7. The uncommon M_3L_2

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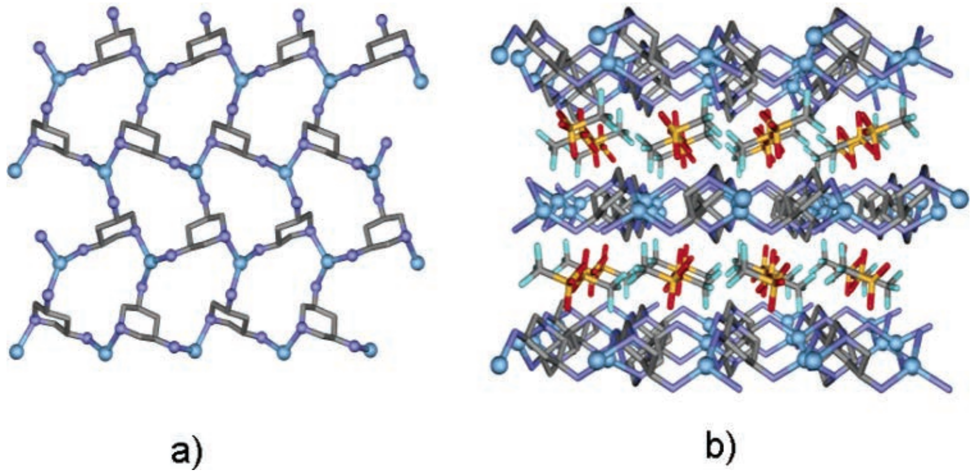

Figure 5. (a) 6^3 honeycomb structure of **6**. (b) View of layer formation of **6** along the crystallographic *a* axis. Hydrogen atoms are removed for clarification. Counterions: oxygen atoms are shown in red, carbon atoms in gray, sulfur atoms in yellow, and fluorine atoms in light blue. Coordination polymer: carbon atoms are represented by gray sticks, Ag(I) ions by large light blue spheres, and nitrogen atoms by small dark blue spheres.

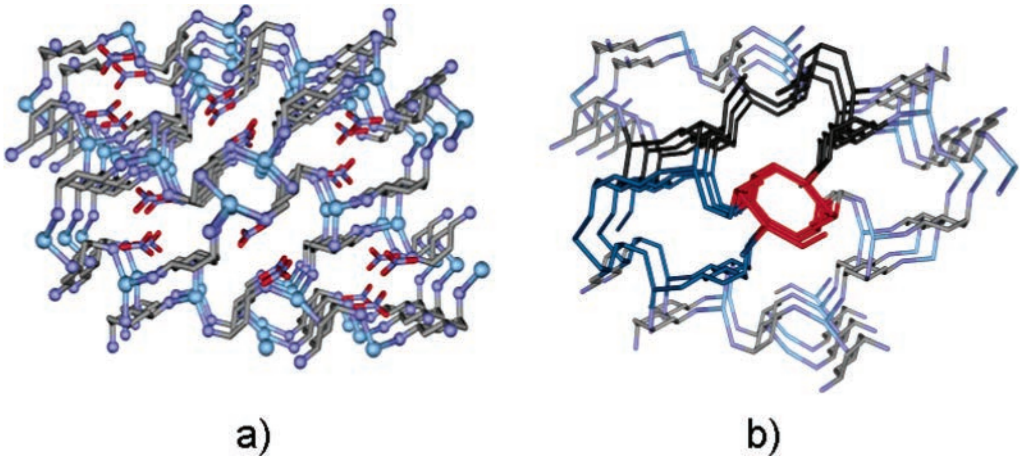

Figure 6. (a) Three-dimensional structure of **7**[12] showing channels along the crystallographic *b* axis, hydrogen atoms are removed for clarification. Oxygen atoms are shown as red and carbon atoms as gray sticks, and Ag(I) ions are represented by large light blue spheres and nitrogen atoms by small dark blue spheres. (b) Open and closed channel formation in **7**. Hydrogen atoms are removed for clarification. The red channel is a right-handed tetragonal channel, the dark blue channel is a left-handed octagonal channel, and the black macrocycles are closed channels within the crystallographic *a*/*c* plane.

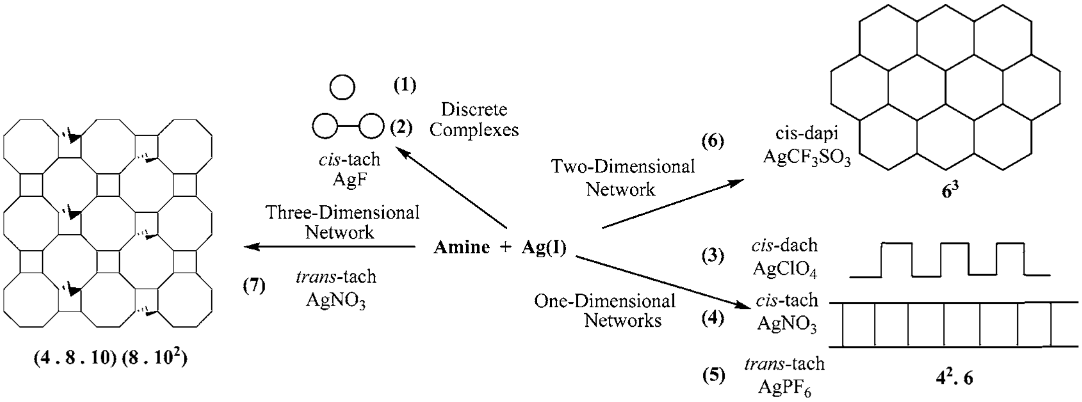

Figure 7. Schematic summary and representation of the range of multidimensional complexes formed by the reaction of rigid amines with a variety of silver(I) salts.

cage structure of compounds **1** and **2** provides a firm basis on which to develop functional, cavity-containing species, and the formation of short Ag···Ag contacts has significant impact on potential applications of the material. The construction of the infinite tubular polymers **4** and **5** from metal−ligand systems that possess a degree of preorganization and a number of arms that can "wrap" is a noteworthy development in nanotube synthesis. We are currently extending this work by investigation into the coordination of these rigid amines with other metal ions and also via derivatization of the amino residues in order to enlarge pore dimensions and increase the functionality of the materials.

Acknowledgment. We thank the EPSRC, the University of Glasgow, the Royal Society, and the Leverhulme Trust for funding.

Supporting Information Available: A detailed description of the hydrogen-bonded networks present in compounds **1** and **2,** the summary of a CSD search of Ag···Ag interactions, and crystallographic data for compounds **1**−**6**, in the form of cif files. This material is available free of charge via the Internet at http://pubs.acs.org.

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