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Different Nuclearity Silver(I) Complexes with Novel Tetracyano Pendant-Armed Hexaazamacrocyclic Ligands

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A new series of different nuclearity silver(I) complexes with a variety of tetracyano pendant-armed hexaazamacrocyclic ligands containing pyridine rings (L^n) has been prepared starting from the nitrate and perchlorate Ag(I) salts in acetonitrile solutions. The ligands and complexes were characterized by microanalysis, conductivity measurements, IR, Raman, electronic absorption and emission spectroscopy, and L-SIMS spectrometry. ^1H NMR titrations were employed to investigate silver complexation by ligands L^3 and $L.^4$ The compounds $[Ag_2L^2(NO_3)_2]$ (**2**), $([Ag_2L^2](ClO_4)_2 \cdot 2CH_3CN)_\infty$ (**4**), $[AgL^3](ClO_4) \cdot CH_3CN$ (**5**), and $[Ag_4(L^4)_2(NO_3)_2](NO_3)_2 \cdot 4CH_3CN \cdot 2H_2O$ (**7**) were also characterized by single-crystal X-ray diffraction. The complexes have different nuclearities. Complex **2** is dinuclear with an $\{AgN_3O_2\}$ core and a significant intermetallic interaction, whereas complex **4** has a polymeric structure formed by dinuclear distorted $\{AgN_4\}$ units joined by nitrile pendant arms. Compound **5** is mononuclear with a distorted $\{AgN_2\}$ linear geometry, and complex **7** consists of discrete units of a tetranuclear array of silver atoms with $\{AgN_3O\}$ and $\{AgN_4\}$ cores in distorted square planar environments. Complexes **2** and **4** were found to be fluorescent in the solid state at room temperature because of the Ag–Ag interactions.

Introduction

Macrocyclic ligand complexes have been extensively studied during the past decades and are often used in catalysis, metalloenzyme, mechanism, and molecular-recognition research.[1] In particular, pendant-armed macrocyclic ligands bearing additional potential ligating groups have long been investigated for the production of endocyclic complexes of low nuclearity with different transition-metal ions for use as, for example, metallobiosites or catalytic reagents.[2] However, pendant arms as the nitrile groups do not allow these units to be involved in the coordination of the encapsulated metal and could promote the formation of polymeric compounds. Recently, nanotubular architectures with cavities or channels of diverse sizes and shapes have

received a great deal of attention because of their applications as technological functional materials.[3,4] In addition, it is well-known that the coordination sphere of Ag(I) is very flexible and can adopt different coordination numbers between 2 and

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Scheme 1
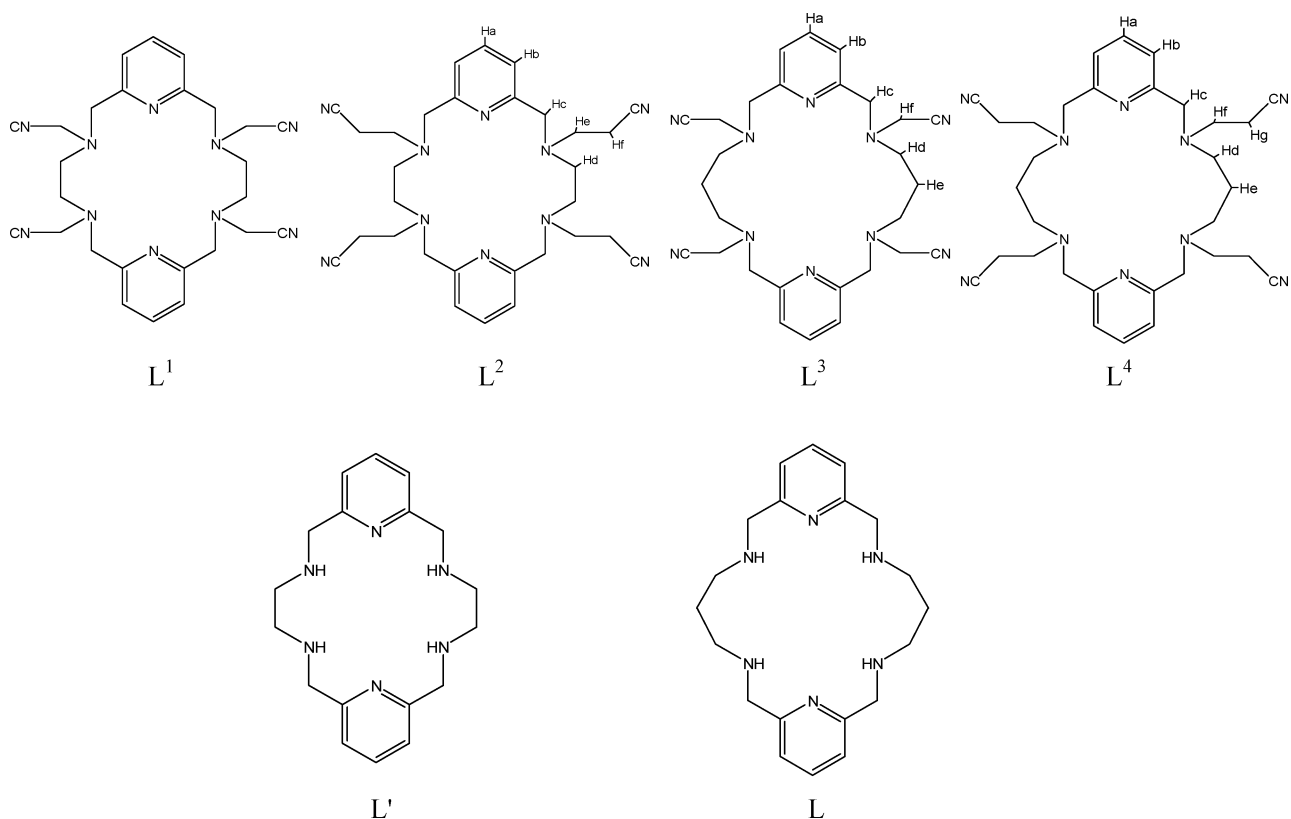
6; it can also give various geometries from linear to tetrahedral, trigonal, and octahedral.[5] Nevertheless, the silver-(I) cation usually prefers a linear, two-coordinate geometry with nitrogen donors.[6] Also, during recent years, there has been a renewed interest in dinuclear and polynuclear Ag(I) complexes, especially because of their luminescence properties and their potential applications in chemical sensors, photochemistry, electroluminescence displays, etc.[7] Although the study of the luminescence properties of Cu(I)[8] and Au-(I)[9] ions is widely acknowledged, polynuclear Ag(I) metal complexes have received little attention, perhaps because of the sensitivity of silver compounds toward photodecomposition; these properties have been established more recently.[10] The presence of structural diversity with direct metal−metal interactions (argentophilicity) seems to be one of the most important factors of such properties.[11]

In a previous publication, we reported the coordination capability of a tetracyanomethylated hexaazamacrocyclic

ligand containing pyridine rings (L[1], Scheme 1) with silver-(I) nitrate and perchlorate salts.[12] It was found that the nitrate complex was dinuclear and the perchlorate derivative presented a polymeric structure because the low coordinative capacity of the counterion causes an intermolecular coordination of the nitrile groups. In this context, we argued that the incorporation of one extra methylene group, in either the cyano pendant arm (L[2]), the tertiary amines on the macrocyclic backbone (L[3]), or both positions (L[4]), to give flexible new ligands could produce a modification in the ligand arrangement and, consequently, in the complex structures.

The work presented here not only highlights an important role for counteranions in the complex structure but also describes the coordination ability of L[2] and the novel pendant-armed macrocyclic ligands L[3] and L[4] to obtain Ag-(I) complexes of different structures and nuclearities.

Results and Discussion

Synthesis and General Characterization. The ligand L[2] was synthesized according to literature methods, and L[3] and L[4] were synthesized in good yield (see Experimental Section) and characterized by elemental analysis, L-SIMS, IR, and ^{1}H NMR spectroscopy. The L-SIMS mass spectra show the parent peaks at 511 and 567 amu for L[3] and L,[4] respectively, which provide evidence for the presence of the macrocyclic ligands.

The ^{1}H NMR spectra of the ligands recorded in deuterated acetonitrile (Table 1, Scheme 1) confirm the integrity of the

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Table 1. ^{1}H NMR Spectra for L[2] and 1:1 Ag(I) Complexes with L[2], for L[3] and [AgL[3]](ClO$_4$)·CH$_3$CN (**5**), and for L[4] and 1:1 Ag(I) Complexes with L[4] in CD$_3$CN[a]

assignment	L[2]	[AgL[2]](X)·nH$_2$O	L[3]	[AgL[3]](ClO$_4$)·CH$_3$CN (**5**)	L[4]	[AgL[4]](X)·nH$_2$O
H$_a$	7.60 (t, 2H)	7.89 (t, 2H)	7.60 (t, 2H)	7.82 (t, 2H)	7.59 (t, 2H)	7.76 (t, 2H)
H$_b$	7.25 (d, 4H)	7.41 (d, 4H)	7.14 (d, 4H)	7.32 (d, 4H)	7.22 (d, 4H)	7.23 (d, 4H)
H$_c$	3.58 (s, 8H)	3.80 (s, 8H)	3.61 (s, 8H)	3.91 (s, 8H)	3.52 (s, 8H)	3.66 (s, 8H)
H$_d$	2.53 (s, 8H)	2.83 (s, 8H)	2.46 (t, 8H)	2.23 (t, 8H)	2.56 (t, 8H)	2.20 (t, 8H)
H$_e$	2.84 (t, 8H)	2.68 (t, 8H)	1.55 (q, 4H)	1.60 (q, 4H)	1.49 (q, 4H)	1.72 (q, 4H)
H$_f$	2.57 (t, 8H)	2.53 (t, 8H)	3.58 (s, 8H)	3.71 (s, 8H)	2.77 (t, 8H)	3.14 (t, 8H)
H$_g$					2.33 (t, 8H)	2.74 (t, 8H)

[a] All values are in parts per million.

molecules and their stability in solution. The spectra show that the four quadrants of the macrocycles are chemically equivalent, as one would expect in this kind of ligand.

To investigate the coordination capability of the ligands toward the Ag(I) ion, we synthesized complexes of L[2], L[3], and L[4] in acetonitrile using hydrated nitrate and perchlorate silver(I) salts in 1:1 and 2:1 Ag:L^n molar ratios. Analytical data are consistent with the formation of 1:1 and 2:1 metal: ligand complexes for L[2] and L[4], but only the mononuclear perchlorate complex could be obtained with L[3], even when the reaction was carried out in a 2:1 metal:ligand molar ratio. Unfortunately, the nitrate complexes with this ligand could not be isolated; all attempts to obtain them as solid compounds were unsuccessful, and a black powder, denoting degradation of the compound, was obtained. The complexes were characterized by elemental analysis, IR and Raman spectroscopy, L-SIMS spectrometry, ^{1}H NMR spectroscopy, and conductivity measurements. The fluorescence properties of some of these complexes were also investigated.

Infrared Spectroscopy. The IR spectra of the silver(I) complexes show similar features. The ν(C≡N) and ν(C≡ C) bands of the pyridine rings are generally shifted to higher wave numbers than those in the free ligand, suggesting coordination of the pyridine groups to the silver ion.[13]

In complexes **4**, **7**, and **9** ([Ag$_2$L[4]](ClO$_4$)$_2$), the ν(C≡N) mode of the pendant groups appears slightly shifted to higher wave numbers compared to those in the corresponding free ligand. This could indicate the presence of nitrile groups coordinated to silver(I) ions, as has been shown in the crystal structures of **4** and **7** (vide infra). Nevertheless, in the other complexes, the ν(C≡N) mode appears at the same position as in the corresponding free ligands, indicating the presence of uncoordinated nitrile groups, as found in the crystal structures of complexes **2** and **5**. In the cases of **2** and **7**, the spectra show the presence of several bands in the region associated with nitrate vibrations. This clearly shows that these complexes contain coordinated nitrate groups.[14] A band at 1380 cm^{-1}, which is associated with the presence of ionic nitrate, is also present in the spectrum of **7**. The mononuclear nitrate complexes exhibit the vibration only at 1380 cm^{-1}, showing that the counterion is not coordinated. The spectra of all nitrate complexes show another band at 2426 cm^{-1}, which can be attributed to the presence of nitrile–nitrate π,π-

interactions, as has been previously described for other nitrate complexes of L[2] [15] and complexes **2** and **7** (vide infra). The IR spectra of the perchlorate complexes feature absorptions attributable to ionic perchlorate at 1100 and 626 cm^{-1}, indicating that these groups are not coordinated to the metal centers in any case.[16]

L-SIMS Spectrometry. L-SIMS mass spectrometry provides key evidence for the formation of the complexes. In all cases, the peak corresponding to the general formula [AgL^n]$^+$ is present, but peaks assigned to higher nuclearity complexes were generally not observed.

Solid UV−Vis and Raman Spectroscopy and Fluorescence Studies. Solid-state UV−vis absorption measurements show that complexes **2** and **4** have small absorptions at 442 and 448 nm, respectively. When theses bands are excited at room temperature, a broad fluorescence emission band in the solid state is observed with a maximum at ca. 565 nm for **2** and 572 nm for **4** (Figure S1, Supporting Information). The bands are similar, showing only a small red-shift of the fluorescence band for **4** relative to the band for **2**. The absorption band is not observed in the spectrum of the free ligand and, as reported previously, the fluorescence properties of the complexes may be due to the $d^{10}-d^{10}$ interactions in the solid state,[17] with the excited state generally being attributed to the metal-based $4d\sigma^* \rightarrow 5p$ transition.[10b] Fluorescence emission was not observed for the other complexes. The complexes do not show fluorescence emission in solution, which indicates a longer Ag−Ag distance than that in the solid state.

Raman spectroscopy studies show an active band at 90 and 100 cm^{-1} for **2** and **4**, respectively, which can also be assigned to the Ag−Ag vibration.[18]

X-ray Diffraction. Slow crystallization from acetonitrile solutions of the complexes gave single crystals of [Ag$_2$L[2]-(NO$_3$)$_2$] (**2**), ([Ag$_2$L[2]](ClO$_4$)$_2$.2CH$_3$CN)$_\infty$ (**4**), [AgL[3]](ClO$_4$)· CH$_3$CN (**5**), and [Ag$_4$L$_2$[4](NO$_3$)$_2$](NO$_3$)$_2$·4CH$_3$CN·2H$_2$O (**7**) that were suitable for X-ray diffraction. Table 2 shows crystal data and structure refinement for **2**, **4**, **5**, and **7**.

Crystal Structure of [Ag$_2$L[2](NO$_3$)$_2$] (2). Recrystallization from acetonitrile of the nitrate silver complex with L[2] in a

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Table 2. Crystal Data and Structure Refinement for [Ag$_2$L^2(NO$_3$)$_2$] (**2**), ([Ag$_2$L^2](ClO$_4$)$_2$·2CH$_3$CN)$_\infty$ (**4**), [AgL^3](ClO$_4$)·CH$_3$CN (**5**), and [Ag$_4$(L^4)$_2$(NO$_3$)$_2$](NO$_3$)$_2$·4CH$_3$CN·2H$_2$O (**7**)

	2	**4**	**5**	**7**
empirical formula	C$_{15}$ H$_{19}$ N$_6$ O$_3$ Ag	C$_{34}$ H$_{44}$ N$_{12}$ O$_8$ Cl$_2$ Ag$_2$	C$_{30}$ H$_{37}$ N$_{11}$ O$_4$ Cl Ag	C$_{36}$ H$_{48}$ N$_{14}$ O$_7$ Ag$_2$
fw	439.23	1035.45	759.03	1004.62
T (K)	293(2)	293(2)	293(2)	293(2)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	*P*21/*n*	*C*2/*c*	*Cc*	*P*21/*n*
a (Å)	9.6001(9)	23.945(4)	18.1456(16)	12.8512(15)
b (Å)	9.3376(8)	7.4886(11)	10.2963(9)	26.383(3)
c (Å)	19.8455(17)	24.771(4)	19.6626(17)	13.1437(16)
β (deg)	102.666(2)	111.612(3)	111.432(2)	94.859(2)
V (Å^3)	1735.7(3)	4129.5(11)	3419.6(5)	4440.3(9)
Z	4	4	4	4
calcd density (Mg/m^3)	1.681	1.665	1.474	1.503
abs coeff (mm^{-1})	1.189	1.142	0.720	0.943
F(000)	888	2096	1560	2048
cryst size (mm^3)	0.21 × 0.16 × 0.11	0.20 × 0.16 × 0.12	0.40 × 0.31 × 0.24	0.35 × 0.33 × 0.31
θ range for data collection (deg)	2.10–28.02	1.77–28.05	2.23–28.03	1.74–28.07
index ranges	−12 ≤ h ≤ 12, −12 ≤ k ≤ 11, −23 ≤ l ≤ 26	−29 ≤ h ≤ 31, −9 ≤ k ≤ 8, −32 ≤ l ≤ 32	−23 ≤ h ≤ 23, −13 ≤ k ≤ 13, −15 ≤ l ≤ 25	−16 ≤ h ≤ 16, −29 ≤ k ≤ 34, −17 ≤ l ≤ 10
no. of reflns collected	9113	11124	10608	25593
no. of independent reflns	3827 [R(int) = 0.0401]	4634 [R(int) = 0.0704]	6104 [R(int) = 0.0306]	10079 [R(int) = 0.0472]
completeness to θ (%)	91.1 (28.02°)	92.5 (28.05°)	96.6 (28.03°)	93.5 (28.07°)
abs correction	empirical	empirical	empirical	empirical
max., min. transmission	0.8803, 0.7883	0.8751, 0.8038	0.8463, 0.7617	0.7587, 0.7338
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/params	3827/0/226	4634/0/263	6104/2/425	10079/0/534
GOF on F^2	0.816	0.811	0.857	0.893
absolute structure param			−0.02(2)	
final R1 indices [$I > 2\sigma(I)$]	0.0469	0.0522	0.0357	0.0504
final wR2 indices [$I > 2\sigma(I)$]	0.0946	0.0960	0.0638	0.1161
R1 indices (all data)	0.1536	0.1634	0.0519	0.1099
wR2 indices (all data)	0.1179	0.1183	0.0676	0.1314
largest diff. peak and hole (e Å^{-3})	0.632 and −0.416	0.807 and −0.747	0.450 and −0.359	1.891 and −1.279

2:1 (Ag:L^2) molar ratio gave colorless monoclinic crystals of [Ag$_2$L^2(NO$_3$)$_2$] (**2**). The molecular structure of the complex is shown in Figure 1a together with the atomic numbering scheme adopted and selected bond distances (Å) and angles (deg).

The structure is centrosymmetric and shows the presence of two metal ions within the cavity of the hexaazamacrocyclic ligand, a situation that gives rise to a dinuclear endomacrocyclic complex. The environment around each silver atom can be described as {AgN$_3$O$_2$} distorted square pyramidal (τ = 0.16), with each metal ion coordinated to one pyridinic nitrogen, two contiguous tertiary amino groups, and two oxygen atoms from an asymmetric bidentate nitrate ion. The distance between the silver atoms, 2.7911(9) Å, is slightly shorter than that in metallic silver, 2.888 Å,[19] indicating an intermetallic interaction and supporting the significance of argentophilicity.[20] The crystal structure is similar to that obtained for [Ag$_2$L^1(NO$_3$)$_2$].[12] The pyridinic nitrogen atom provides the strongest bond to the silver atom (Ag−N$_{py}$ = 2.389(4) Å, Ag−N$_{am}$ = 2.444(4) and 2.471(4) Å).

The macrocyclic ligand is neither folded nor twisted. The disposition is quite planar; the pyridyl groups lie parallel to one another, and the planes containing those rings are 1.27 Å a way from each other. The dihedral angle between the
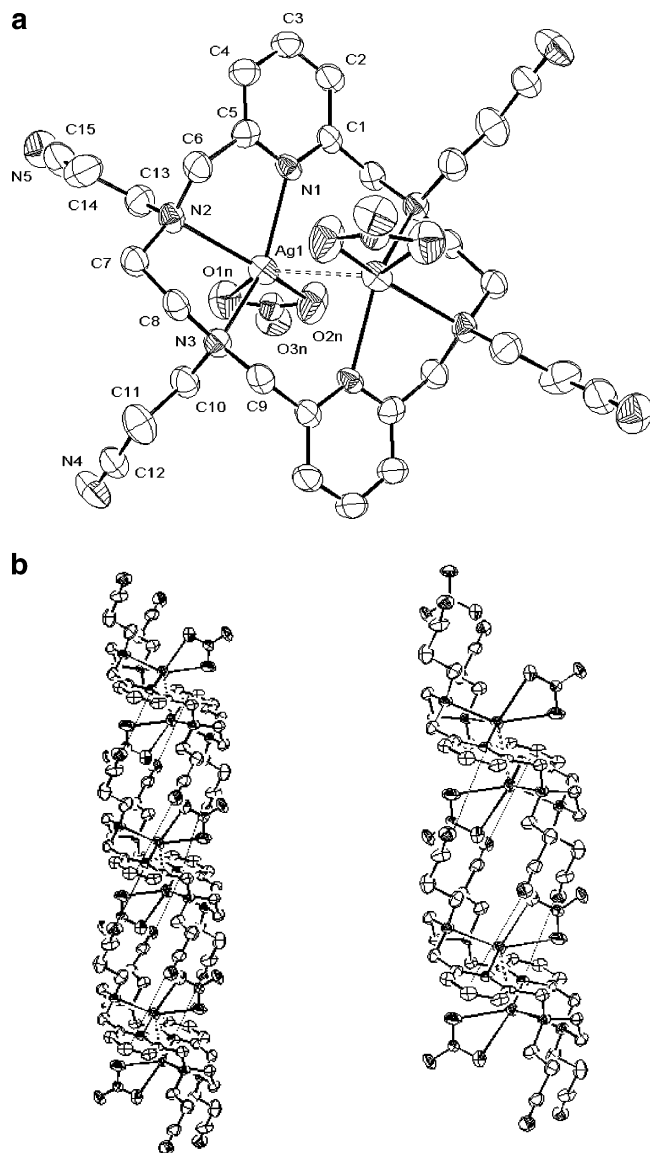
pyridine ring and the plane containing the four aliphatic nitrogen atoms of the ligand backbone is 28.8°. The silver atoms are situated 0.8224 Å above and below the best plane defined by the six donor nitrogen atoms of the ligand backbone (rms 0.0954) because of the coordination of the nitrate groups.

Despite the known high affinity of cyano groups toward Ag$^+$ ions,[21] the cyano pendant groups in this compound are not involved in metal coordination; those attached to contiguous tertiary amine nitrogen atoms lie on the same side of the large ring and not on opposite sides, a situation in contrast to that in free ligand L^2. A partial view of the unit cell along the *a*-axis (Figure 1b) shows that the coordinated nitrate groups lie parallel between the nitrile groups at ca. 4.3 Å, indicating the existence of a certain π,π-interaction between them. A similar situation has previously been observed in other complexes with this type of ligand.[15] In addition, it can be seen that these nitrile groups are directed toward the pyridyl groups of neighboring molecules in the unit cell, with distances of 3.58 and 4.41 Å between the centroid of a pyridine ring and the nitrogen atom of the cyano groups. This interaction can be explained as a complexation by the metal ions that would make the pyridine ring essentially electron deficient and act as a σ-acceptor or π-acceptor.[22] On the other hand, even the nitrile group has

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The complex [Ag$_2$L^1(NO$_3$)$_2$] did not show these intermolecular interactions. This different behavior is probably related to the presence of an additional methylene group in the pendant arms. The increase in the length of the cyano pendant arms allows the molecules to be joined through these intermolecular interactions, a situation that is not possible for [Ag$_2$L^1(NO$_3$)$_2$].

Crystal Structure of ([Ag$_2$L^2](ClO$_4$)$_2$·2CH$_3$CN)$_\infty$ (4). Recrystallization from acetonitrile of the perchlorate silver complex with L^2 in a 2:1 (Ag:L^2) molar ratio gave colorless monoclinic crystals of ([Ag$_2$L^2](ClO$_4$)$_2$·2CH$_3$CN)$_\infty$ (4). The molecular structure is shown in Figure 2a together with the atomic numbering scheme adopted. For the sake of clarity, a view of the macrocycle is represented in Figure 2b together with selected bond distances (Å) and angles (deg).

As in the nitrate complex discussed above (2), the crystal structure of ([Ag$_2$L^2](ClO$_4$)$_2$·2CH$_3$CN)$_\infty$ (4) shows the presence of two metal atoms within the macrocyclic backbone; however, in this case, the geometry of the donor atoms around the silver atoms could be described as very distorted square planar {AgN$_4$}, with each silver atom coordinated to one pyridinic nitrogen, two contiguous tertiary amine nitrogens, and one nitrogen atom from a nitrile group belonging to a neighboring macrocyclic ligand. The rms value for the plane N1–N2–N3–N4 is 0.674, and Ag(1) is 0.17 Å away from this plane. In this case, the counterions do not interact with the metal ions, and the intermolecular interactions between the metal ion and the nitrile groups give rise to a one-dimensional stairlike polymer structure along the *b*-axis with a pitch of 7.489 Å. The Ag–Ag distance is 2.9992(12) Å, which is longer than that in metallic silver but significantly less than twice the van der Waals radius for silver (3.44 Å),[19] indicating (as in 2) a certain intermetallic interaction. This intermetallic distance is smaller than that in the corresponding perchlorate complex with L^1 (4.718 Å), which showed the metal atoms in a five-coordination sphere bonded by a pyridinic nitrogen, two alternate tertiary amines, and two different nitrile groups to give a 2D polymeric structure.[12]

The Ag–N$_{am}$ distances are similar to those in the related nitrate complex 2 but the Ag–N$_{py}$ distance (2.310(18) Å) is slightly shorter, as one would expect with a lower coordination number. The macrocyclic ligand is neither folded nor twisted. The dihedral angle between the pyridyl groups is 0°, with the average distance between the head pyridine rings of a macrocyclic molecule being approximately 1.6 Å. The dihedral angles between the rings and the plane containing the four aliphatic nitrogen atoms (rms 0.00) of the ligand backbone are 33.32°, which is significantly smaller than the angles in the perchlorate silver complex with L^1 (90°). The coordination of the nitrile pendant groups from another ligand molecule to the metal produces displacements of 0.88875 Å outside this plane for Ag(1). The nonbonded cyano pendant groups are directed toward the pyridyl rings of neighboring ligand molecules at ca. 3.5 Å (Figure 2c), as occurred in 2.

A cell view along the *b*-axis shows how the polymeric structure displays a tubular architecture in 1D (Figure 2d) with the silver atoms situated in the central cavity. The

Figure 1. (a) Crystal structure and selected bond lengths (Å) and angles (deg) for [Ag$_2$L^2(NO$_3$)$_2$] (2). Ag(1)–N(1), 2.389(4); Ag(1)–N(2), 2.471-(4); Ag(1)–N(3), 2.444(4); Ag(1)–O(2N), 2.538(5); Ag(1)–O(1N), 2.545-(5); Ag(1)–Ag(1)#1, 2.7911(9); N(1)–Ag(1)–N(3), 130.77(15); N(1)–Ag(1)–N(2), 73.03(16); N(3)–Ag(1)–N(2), 75.27(15); N(1)–Ag(1)–O(1N), 116.54(16); N(1)–Ag(1)–O(2N), 105.85(18); N(3)–Ag(1)–O(1N), 105.05(16). #1: −*x*, −*y* + 1, −*z* + 1. (b) Different perspective view of complex 2 showing the intermolecular nitrile–py interactions along the *a*-axis.

a potential π-donor character (side-on fashion), although it usually acts as a weak σ-donor (end-on fashion) or π-acceptor.[23] In this case, the dihedral angles between nitrile groups and pyridyl rings (66 and 67°) mean that the arrangement is best described as an end-on or point-to-face T-shaped conformation between the lone pair orbital on the N atom of the cyano pendant groups and the pyridine system rather than a side-on arrangement.

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(23) (a) Wilkinson, G. *Comprehensive Coordination Chemistry II*; Pergamon: Oxford, U.K., 2003; Vol. 2; p 261. (b) Howell, J. A. S.; Saillard, J.-Y.; Le Beuze, A.; Jaouen, J. *J. Chem. Soc., Dalton Trans.* **1982**, 2533.
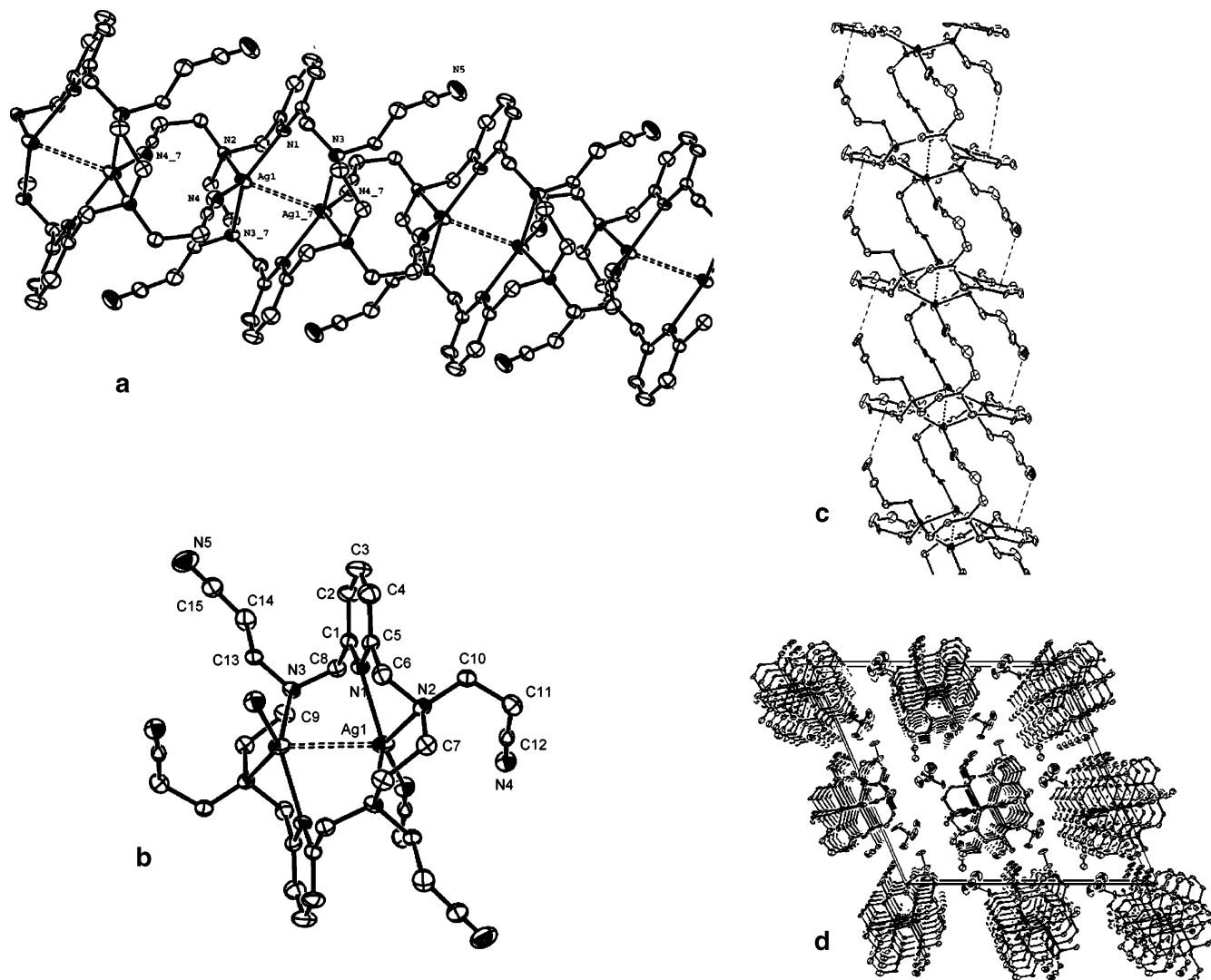
Figure 2. (a) Crystal structure along the *b*-axis of the polymeric complex ([Ag$_2$L^2](ClO$_4$)$_2$·2CH$_3$CN)$_\infty$ (**4**). (b) Representation of asymmetric unit for **4** together with selected bond lengths (Å) and angles (deg). N(1)−Ag(1), 2.301(5); N(2)−Ag(1), 2.522(5); N(3)−Ag(1)#1, 2.478(4); N(4)−Ag(1), 2.229(6); Ag(1)−Ag(1)#1, 2.9992(12); N(4)−Ag(1)−N(1), 128.02(18); N(4)−Ag(1)−N(3)#1, 103.71(17),; N(1)−Ag(1)−N(3)#1, 127.15(16); N(4)−Ag(1)−N(2), 138.03(19); N(1)−Ag(1)−N(2), 74.07(16); N(3)#1−Ag(1)−N(2), 73.98(15); N(4)−Ag(1)−Ag(1)#1, 98.73(15); N(1)−Ag(1)−Ag(1)#1, 74.46(12); N(3)-#1−Ag(1)−Ag(1)#1, 89.29(12); N(2)−Ag(1)−Ag(1)#1, 122.86(12). #1: −*x* + 3/2, −*y* + 3/2, −*z*; #2: −*x* + 3/2, −*y* + 5/2, −*z*. (c) Perspective view of complex **4** showing the intermolecular nitrile−py interactions along the *b*-axis. (d) A stereoview of the unit cell along the *b*-axis for **4** showing the tubular arrangement and the packing of the chains in the crystal.

perchlorate groups and acetonitrile molecules that do not have contact with the metal ions reside outside the channels.

Therefore, by simply altering the pendant-arm length from methylnitrile (L^1) to ethylnitrile (L^2), a different network motif for the resulting coordination polymer with perchlorate Ag(I) is obtained.

Crystal Structure of [AgL^3](ClO$_4$)·CH$_3$CN (5). The product obtained in the synthesis of the Ag(I) perchlorate complex with ligand L^3 in a 1:1 (Ag:L^3) molar ratio was found to be [AgL^3](ClO$_4$)·CH$_3$CN (**5**). The molecular structure of this complex is shown in Figure 3 along with the atom numbering scheme and selected bond distances (Å) and angles (deg).

In this case, the complex is mononuclear with the metal located within the cavity of the macrocyclic backbone and coordinated only to the pyridine nitrogen atoms Ag−N(1) (2.240(4) Å) and Ag−N(4) (2.227(3) Å). The geometry of

the Ag(I) ion can therefore be considered as {AgN$_2$} slightly distorted linear, N(1)−Ag−N(4) = 175.61°. The structure is completed by a perchlorate counterion and one acetonitrile molecule from the solvent, neither of which are coordinated to the metal.

A CSD search revealed that this is one of the few cases in which these types of aza- or oxaazamacrocycles containing pyridine ring ligands give a mononuclear complex with Ag-(I) and is the first example of such a complex with a linear geometry. To the best of our knowledge, only Kumar et al.[24] have described a mononuclear complex of Ag(I) with an 18-membered oxaazamacrocyclic ligand and, in this case, the metal ion is coordinated by two pyridyl groups and a bidentate nitrate ion.

(24) Kumar, S.; Hundal, M. S.; Hundal, G.; Kaur, N.; Singh, H. *Tetrahedron* **1997**, *31*, 10841.
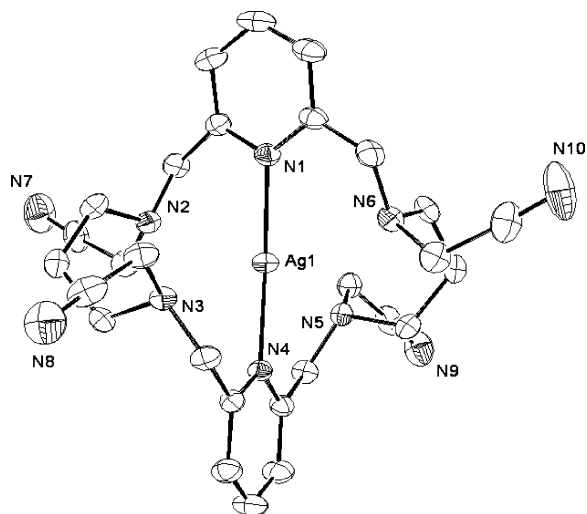
Figure 3. Molecular structure and selected bond lengths (Å) and angles (deg) of [AgL^3](ClO$_4$)·CH$_3$CN (**5**). Ag(1)−N(1), 2.240(4); Ag(1)−N(4), 2.227(3); N(1)−Ag(1)−N(4), 175.61(13).

The tertiary amine nitrogen atoms are situated at distances that vary from 2.661 to 2.788 Å; these distances are longer than those found in similar silver complexes with tertiary amines[25] and too long to be considered bond distances. However, these distances could be indicative of certain interactions, as described by Fenton et al.[26] The other distances and angles do not warrant further comment.

The macrocyclic ligand is not folded but presents a "twist−wrap" conformation around the metal ion by twisting the pyridyl bridgehead units relative to each other. This gives rise to a helical shape with a rotation angle between pyridine rings of 76°.

The increase in the length of the aliphatic chain on the macrocyclic skeleton by one methylene group on changing from ethylene to propylene (a change that increases the size of the hole in the macrocyclic ligand) produces a decrease in the nuclearity of the complex.

The nitrile groups are not involved in intermolecular bonding. This is a significant difference with respect to the silver perchlorate complexes of L^1 and L^2 discussed above.

Crystal Structure of [Ag$_4$(L^4)$_2$(NO$_3$)$_2$](NO$_3$)$_2$·4CH$_3$CN· 2H$_2$O (7). The crystal structure of the silver nitrate complex with macrocyclic ligand L^4 in a 2:1 (Ag:L^4) molar ratio was also studied by X-ray diffraction. The molecular structure of [Ag$_4$(L^4)$_2$(NO$_3$)$_2$](NO$_3$)$_2$·4CH$_3$CN·2H$_2$O (**7**) is shown in Figure 4 together with the atomic numbering scheme adopted and selected bond distances (Å) and angles (deg).

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(26) (a) Adams, H.; Bailey, N. A.; Dwyer, M. J. S.; Fenton, D. E.; Hellier, P. C.; Hempstead, P. D.; Latour, J. M. *J. Chem. Soc., Dalton Trans.* **1993**, 1207. (b) Adams, H.; Bailey, N. A.; Carlisle, W. D.; Fenton, D. E.; Rossi, G. *J. Chem. Soc., Dalton Trans.* **1990**, 1271.
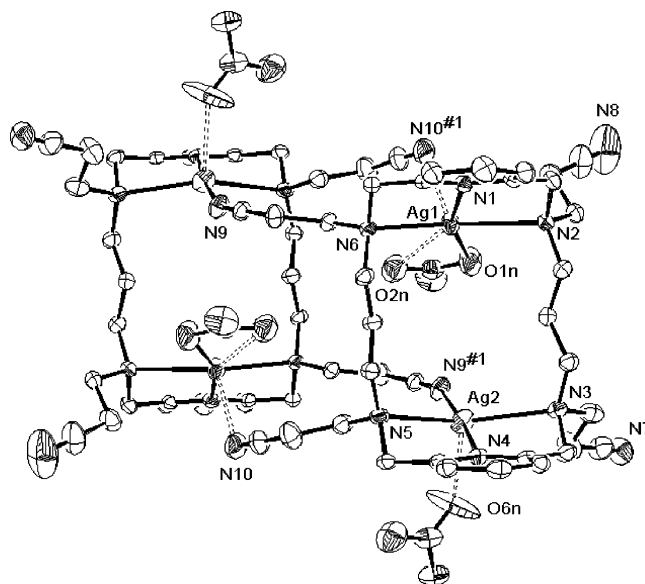
Figure 4. Crystal structure and selected bond lengths (Å) and angles (deg) of [Ag$_4$(L^4)$_2$(NO$_3$)$_2$](NO$_3$)$_2$·4CH$_3$CN·2H$_2$O (**7**). N(1)−Ag(1), 2.301(5)N-(2)−Ag(1) 2.522(5); N(3)−Ag(1)#1, 2.478(4); N(4)−Ag(1), 2.229(6); Ag-(1)−Ag(1)#1, 2.9992(12); N(4)−Ag(1)−N(1), 128.02(18); N(4)−Ag(1)−N(3)#1, 103.71(17); N(1)−Ag(1)−N(3)#1, 127.15(16); N(4)−Ag(1)−N(2), 138.03(19); N(1)−Ag(1)−N(2), 74.07(16); N(3)#1−Ag(1)−N(2), 73.98-(15); N(4)−Ag(1)−Ag(1)#1, 98.73(15); N(1)−Ag(1)−Ag(1)#1, 74.46(12); N(3)#1−Ag(1)−Ag(1)#1, 89.29(12); N(2)−Ag(1)−Ag(1)#1, 122.86(12). #1: −x + 3/2, −y + 3/2, −z; #2 −x + 3/2, −y + 5/2, −z.

The complex presents a tetranuclear structure that has crystallographically imposed symmetry in the unit cell. The structure can be considered as being formed by two dinuclear silver(I) complexes interacting with each other through the cyano pendant groups to give tetrameric units. The metal atoms are situated on the vertex of a planar rhomboid with Ag−Ag−Ag angles of 77.25 and 102.75°.

The silver atoms have different environments. Ag(1) has a {AgN$_3$O} core and is bonded to one pyridinic group and two alternate tertiary amine nitrogens; the fourth position is occupied by an oxygen atom of a nitrate anion (Ag(1)−O(1n) = 2.388(5) Å), with another oxygen atom presenting a nonbonding interaction (Ag(1)−O(2n) = 2.813 Å).[27] Thus, the coordination geometry can be considered as being distorted square planar ($\sum_{Ag}$ = 358.74°, rms 0.2123), with the Ag(1) atom situated 0.2633 Å out of that plane because of a weak contact with a cyano pendant group of the other macrocyclic ligand directed toward the silver atom (Ag(1)−N(10) = 2.818 Å).[28] This nitrile group lies parallel to the coordinated nitrate group at ca. 3.4 Å, a situation that also indicates a certain π,π-interaction between them, as found in the crystal structure of **2** described above.

The second silver atom, Ag(2), has a {AgN$_4$} core that also has a distorted square planar geometry. This is bonded to the other pyridine nitrogen, two alternate tertiary amines

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of the macrocyclic ligand, and a cyano group from a pendant arm of the neighboring ligand molecule ($\sum_{Ag} = 359.73°$, rms 0.2944). The silver atom is 0.2938 Å out of this plane because of interaction with an oxygen of a monodentate nitrate counterion (Ag(2)−O(6n) = 2.618 Å).[29] The other cyano pendant-arm groups are not coordinated and are directed outward to the same side of the main macrocyclic hole from the macrocyclic backbone.

The nitrogen atom of the coordinated cyano pendant arm provides the strongest bond to the silver atoms (Ag(2)−N(9)-#1 = 2.215(4) Å), and the distances between the pyridinic nitrogen atoms and the metal ion (Ag(1)−N(1) = 2.313(3) Å and Ag(2)−N(4) = 2.270(3) Å) are in the range expected for this type of bond. The bond distances between the tertiary amine nitrogen and the silver atoms vary in the range 2.585-(3)−2.637(4) Å, which is significantly longer than that in the other complexes discussed above.

Neither of the macrocyclic ligand molecules is twisted as in **5** but they are completely folded. In this disposition, the pyridine rings of a macrocyclic ligand are parallel to one another (dihedral angle of 7.88°) and perpendicular to the plane described for the tertiary amine nitrogen (dihedral angles of 84.65 and 87.56°).

NMR Studies. ^{1}H NMR titrations were employed to investigate silver complexation by L[2], L[3], and L[4] in CD[3]-CN, and the log β values for silver(I) complexation with L[3] and L[4] were determined using a local version of the program WinEQNMR.[30]

Stability constants can be determined by NMR spectroscopy when the species are in rapid exchange on the NMR time scale and when there is a variation in the chemical shift of a suitable nucleus on formation of the complex species. The addition of silver salts to a CD[3]CN solution of L[2] was found to give a spectrum showing signals from free and complexed ligand, indicating that ligand exchange is slow on the time scale of the NMR experiment; in this case, the log β values for silver(I) complexation with L[2] could not be determined.

^{1}H NMR titration of L[2] with nitrate or perchlorate silver salts (Table 1 and Figure S3 of the Supporting Information) shows that the incremental addition of Ag(I) salt gives rise to the downfield shift of most proton signals of the molecule until the 1:1 relation is reached and signals from free and complexed ligand signals can be observed. Only H[e] and H[f] signals are slightly upfield shifted, showing the noncoordination of the pendant groups in solution. The addition of more Ag(I) salt (greater than the 2:1 relation) gives rise to a more complicated spectrum that shows the presence of two different compounds in solution, probably the mono- and dinuclear species. Crystallization of compounds **2** and **4** can be observed in a few hours.

Nevertheless, for L[3] and L[4], the species are in rapid exchange on the NMR time scale; the change in the downfield chemical shift of the *p*-pyridine protons (H[a]) in

the macrocyclic ring was monitored throughout the titration. The induced chemical shift corresponding to each addition of silver ions was then plotted against the ratio of metal ion concentration to ligand concentration present in the NMR tube.

Titration curves for the incremental addition of silver(I) nitrate or perchlorate to L[3] and L[4] yielded clear 1:1 (metal: ligand) end points, indicating that it is mainly the 1:1 complex present in solution (Figures S2 and S3, Supporting Information). Analysis of these curves allowed the corresponding log β_1 values to be calculated for Ag(I) complexation. The values obtained for L[3] were log $\beta_1 = 5.04$ for the nitrate complex and log $\beta_1 = 4.88$ for the perchlorate complex. In the case of L[4], the values were log $\beta_1 = 6.04$ for the nitrate and log $\beta_1 = 5.16$ for the perchlorate. Thus, in both cases, the log β_1 values obtained are slightly higher for the nitrate than for the perchlorate complexes, and the increase by one methylene group in the cyano pendant group (from L[3] to L[4]) gives rise to a slight increase in the log β value for silver(I) complexation.

It is worth noting that the addition of large amounts of silver(I) to L[4] (up to 2:1 metal:ligand ratio) only gave slight upfield shifts in the *p*-pyridine proton signals in the NMR spectra, indicating the formation of the 2:1 metal:ligand compounds. Nevertheless, for L[3], no change was observed.

The ^{1}H NMR data for the 1:1 silver(I) complexes are listed in Table 1. The assignments for the spectra correspond to the labeling shown in Scheme 1. In the L[3] and L[4] silver complexes, as in the free ligands, the four quadrants of the macrocycles are chemically equivalent, and only one pattern is observed for each of the protons H[a]−H[g]. In all cases, most of the proton resonances are shifted downfield in comparison with those in the free ligand, showing coordination of the ligand to the metal. Only H[d] protons from the propylene chains are shifted upfield.

The ^{1}H NMR spectra of the 1:1 nitrate and perchlorate complexes were identical, indicating that the complexes have similar structures in solution.

Molar Conductivity Studies. The molar conductivities of the complexes in DMF fall within the range reported for 1:1 electrolytes for the mononuclear complexes or 2:1 electrolytes for the dinuclear ones, showing that the counterions are not coordinated to the metal in solution.[31]

Conclusion

In summary, the present work describes the synthesis and characterization of three (two of which are novel) pendant-armed hexaazamacrocyclic ligands and their nitrate and perchlorate silver(I) complexes in 1:1 and 2:1 (Ag:L[n]) molar ratios. The ligands bear four cyano pendant-arm groups, which are not involved in the coordination of the encapsulated metal ion and could promote the formation of high nuclearity compounds. The reaction of silver(I) nitrate or perchlorate salts with these pendant-armed macrocyclic ligands (L[2], L[3], and L[4]) led to the formation of complexes characterized by 1:1 or 2:1 metal:ligand ratios for L[2] and

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L[4]. For L[3], only the mononuclear complex [AgL[3]](ClO$_4$)·CH$_3$-CN (**5**) was obtained.

The different metal environments, as well as the structures of the complexes obtained, were found to depend on the nature of the counterion as well as the macrocyclic backbone and the length of the cyano pendant arms. Thus, complexes of different nuclearities (from mononuclear to polymer) and with a variety of coordination environments for Ag(I) ions were obtained. The complexes [Ag$_2$L[2](NO$_3$)$_2$] (**2**) and ([Ag$_2$L[2]](ClO$_4$)$_2$·2CH$_3$CN)$_\infty$ (**4**) present a supramolecular structure with a tubular arrangement supported by the interaction between the pyridyl ring and nitrile pendant groups. Absorption and emission studies revealed that both complexes are fluorescent in the solid state at room temperature because of the existence of Ag−Ag interactions.

Complexes [AgL[3]](ClO$_4$)·CH$_3$CN (**5**) and [Ag$_4$(L[4])$_2$(NO$_3$)$_2$]-(NO$_3$)$_2$·4CH$_3$CN·2H$_2$O (**7**) are formed by mononuclear and tetranuclear discrete molecules, respectively.

Therefore, it can been seen that a simple modification in the length of the chain between the tertiary amine groups of the ligands and also in the cyano pendant-arm groups, together with the presence of nitrate or perchlorate counterions, leads to silver complexes with different nuclearity. The nitrate silver complexes with L[1] and L[2] are dinuclear (with the counterions acting as bidentate units and the pendant groups not coordinated). In contrast, the 2:1 silver:ligand molar ratio nitrate complex with L[4] is tetranuclear, with some of the cyano pendant arms coordinated and the nitrate groups acting as monodentate units. In the perchlorate complexes, the counterions are not coordinated to the metal in any case. The silver(I) complex with L[3], which has the short pendant groups, presents a mononuclear character, whereas the complex with ligand L[2], which has the cyanoethyl pendant group, gives a dinuclear linear polymeric structure.

Experimental Section

Chemicals and Starting Materials. L, L′, and L[2] were synthesized according to literature methods.[15,32] 2,6-Pyridinedimethanol, ethylenediamine, bromoacetonitrile, acrylonitrile, and hydrated nitrate and perchlorate silver(I) salts were commercial products (from Alfa and Aldrich) and used without further purification. Solvents were of reagent grade and purified by standard methods. *Caution: Although problems were not encountered during the course of this work, attention is drawn to the potentially explosive nature of perchlorates.*

Measurements. Elemental analyses were performed on a Carlo-Erba EA microanalyzer. IR spectra were recorded as KBr disks on a Bruker IFS-66V spectrophotometer. L-SIMS spectra were recorded using a Micromass Autospec spectrometer with 3-nitrobenzyl alcohol as the matrix. Conductivity measurements were carried out in 10^{-3} mol dm^{-3} DMF solutions at 20 °C using a WTW LF3 conductivimeter. ^{1}H NMR spectra were recorded on a Bruker 500 MHz spectrometer using CD$_3$CN as the solvent. Raman spectra were recorded on a FT Bruker Ramanscope spectrophotometer. Solid-state absorption spectra were obtained using a Hitachi 4-3200 spectrophotometer with MgCO$_3$ as the reference. Emission spectra were obtained on a SPEX Fluoromax spectrophotometer.

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NMR Titrations. NMR titrations were employed to investigate silver complexation by ligands L[3] and L[4]. Titrations were performed by sequential 10 μL additions of silver(I) solution (≈0.05 M) in CD$_3$CN to a solution of the ligand (≈0.02 M) in the same solvent as that contained in the NMR tube. For each system, the change in the chemical shift of the *p*-pyridine protons in the macrocyclic ring was monitored throughout the titration. The induced chemical shift corresponding to each addition of silver ion was then plotted against the ratio of metal ion concentration to ligand concentration present in the NMR tube. The NMR titration data were analyzed using a local version of the program WinEQNMR. This program is used to evaluate stability constants in systems in which the species are in rapid equilibrium and the NMR chemical shift data reflect the degree of complex formation. The program fits a titration curve to the measured data using an iterative process that starts with initial estimates of the stepwise stability constants.

Preparation of the Ligands. Synthesis of L[3]. L[3] was synthesized by modifying a previously reported method for L[1].[12] A solution of L (3 mmol, 1.06 g) in acetonitrile (100 mL) was heated under reflux and bromoacetonitrile (15 mmol, 2.46 g) and Na$_2$CO$_3$ (35 mmol, 3.71 g) were added. The mixture was heated under reflux for 18 h and filtered; the filtrate was then evaporated to dryness. The residue was extracted with water/chloroform. The organic layer was dried over anhydrous MgSO$_4$ and evaporated to yield an orange solid, which was recrystallized from acetonitrile to give ligand L[3] as a white solid. Anal. Calcd for C$_{28}$H$_{34}$N$_{10}$ (MW 510.64): C, 65.8; H, 6.7; N, 27.4. Found: C, 65.7; H, 6.8; N, 27.4. Yield: 63%. IR (KBr, cm^{-1}): 1588, 1577, 1460, 1434 (ν(C=C)$_{ar}$ and ν(C=N)$_{py}$), 2227 (ν(C≡N)). MS (L-SIMS, *m/z*): 511 amu [L[3]H]$^+$. Color: white.

Synthesis of L[4]. L[4] was synthesized by following the method previously reportedfor L[2].[15] A solution of L (3 mmol, 1.06 g) in acrylonitrile (30 mL) was heated under reflux for 24 h. The solution was filtered, and the filtrate was evaporated to dryness. The residue was extracted with water/chloroform. The organic layer was dried over anhydrous MgSO$_4$ and evaporated to yield an orange solid, which was recrystallized from acetonitrile to give ligand L[4] as a white solid. Anal. Calcd for C$_{32}$H$_{42}$N$_{10}$ (MW 566.75): C, 67.8; H, 7.4; N, 24.7. Found: C, 67.7; H, 7.6; N, 24.6. Yield: 70%. IR (KBr, cm^{-1}): 1590, 1573, 1462, 1431 (ν(C=C)$_{ar}$ and ν(C=N)$_{py}$), 2245 (ν(C≡N)). MS (L-SIMS, *m/z*): 567 amu [L[4]H]$^+$. Color: white.

Synthesis of the Metal Complexes. General Procedure. A solution of the nitrate or perchlorate silver(I) salt (0.25 or 0.5 mmol) in acetonitrile (5 mL) was added to a solution of the appropriate ligand (0.25 mmol) in acetonitrile (20 mL), and the resulting solution was stirred for 1 h. The solution was concentrated to ca. 10 mL and allowed to stand at room temperature until the product crystallized. The products were dried under vacuum and recrystallized from acetonitrile.

[AgL[2]](NO$_3$)·5H$_2$O (1). Anal. Calcd for C$_{30}$H$_{48}$N$_{11}$O$_8$Ag (MW 798.7): C, 45.1; H, 6.0; N, 19.3. Found: C, 44.9; H, 6.1; N, 19.3. Yield: 62%. IR (KBr, cm^{-1}): 1599, 1578, 1471, 1458 (ν(C=N)$_{py}$ and ν(C=C)), 2426, 2246 (ν(C≡N)), 1380 (ν(NO$_3^-$)). MS (L-SIMS, *m/z*): 645 amu [AgL[2]]$^+$. Λ$_M$ (Ω^{-1} cm^2 mol^{-1}, in DMF): 72 (1:1). Color: white.

[Ag$_2$L[2](NO$_3$)$_2$] (2). Anal. Calcd for C$_{30}$H$_{38}$N$_{12}$O$_6$Ag$_2$ (MW 878.4): C, 41.0; H, 4.4; N, 19.1. Found: C, 41.0; H, 4.6; N, 19.2. Yield: 55%. IR (KBr, cm^{-1}): 1600, 1579, 1473, 1461 (ν(C=N)$_{py}$ and ν(C=C)), 2426, 2245 (ν(C≡N)), 1449, 1303, 821 (ν(NO$_3^-$)). MS (L-SIMS, *m/z*): 645 amu [AgL[2]]$^+$. Λ$_M$ (Ω^{-1} cm^2 mol^{-1}, in DMF): 180 (2:1). Color: white.

[AgL²](ClO₄)·4H₂O (3). Anal. Calcd for $C_{30}H_{46}N_{10}ClO_8Ag$ (MW 818.1): C, 44.1; H, 5.6; N, 17.1. Found: C, 43.9; H, 5.8; N, 16.8. Yield: 70%. IR (KBr, cm⁻¹): 1600, 1578, 1470, 1459 (ν(C=N)$_{py}$ and ν(C=C)), 2245 (ν(C≡N)), 1100, 626 [ν(ClO₄⁻)]. MS (L-SIMS, m/z): 645 amu [AgL²]⁺. Λ_M (Ω^{-1} cm² mol⁻¹, in DMF): 78 (1:1). Color: white.

([Ag₂L²](ClO₄)₂·2CH₃CN)∞ (4). Anal. Calcd for $C_{34}H_{44}N_{12}O_8$-Cl_2Ag_2 (MW 1035.4): C, 39.4; H, 4.3; N, 16.2. Found: C, 39.2; H, 4.3; N, 16.0. Yield: 46%. IR (KBr, cm⁻¹): 1600, 1578, 1471, 1463 (ν(C=N)$_{py}$ and ν(C=C)), 2250 (ν(C≡N)), 1100, 626 (ν(ClO₄⁻)). MS (L-SIMS, m/z): 645 amu [AgL²]⁺. Λ_M (Ω^{-1} cm² mol⁻¹, in DMF): 136 (2:1). Color: white.

[AgL³](ClO₄)·CH₃CN (5). Anal. Calcd for $C_{28}H_{37}N_{11}O_4ClAg$ (MW 759.0): C, 47.5; H, 4.9; N, 20.3. Found: C, 47.3; H, 4.8; N, 20.2. Yield: 72%. IR (KBr, cm⁻¹): 1588, 1577, 1459, 1450 (ν-(C=N)$_{py}$ and ν(C=C)), 2227 (ν(C≡N)), 1100, 626 (ν(ClO₄⁻)). MS (L-SIMS, m/z): 617 amu [AgL³]⁺. Λ_M (Ω^{-1} cm² mol⁻¹, in DMF): 73 (1:1). Color: white.

[AgL⁴](NO₃) (6). Anal. Calcd for $C_{32}H_{42}N_{11}O_3Ag$ (MW 736.6): C, 52.2; H, 5.7; N, 20.9. Found: C, 52.1; H, 5.7; N, 21.0. Yield: 55%. IR (KBr, cm⁻¹): 1600, 1575, 1472, 1460 (ν(C=N)$_{py}$ and ν(C=C)), 2426, 2246 (ν(C≡N)), 1380 (ν(NO₃⁻)). MS (L-SIMS, m/z): 673 amu [AgL⁴]⁺. Λ_M (Ω^{-1} cm² mol⁻¹, in DMF): 68 (1:1). Color: white.

[Ag₄(L⁴)₂(NO₃)₂](NO₃)₂·4CH₃CN·2H₂O (7). Anal. Calcd for $C_{72}H_{100}N_{28}O_{14}Ag_4$ (MW 2013.2): C, 43.0; H, 5.0; N, 19.5. Found: C, 42.6; H, 4.8; N, 19.2. Yield: 42%. IR (KBr, cm⁻¹): 1590, 1573, 1462, 1450 (ν(C=N)$_{py}$ and ν(C=C)), 2426, 2250 (ν(C≡N)), 1430, 1383, 1319, 820 (ν(NO₃⁻)). MS (L-SIMS, m/z): 673 amu [AgL⁴]⁺. Λ_M (Ω^{-1} cm² mol⁻¹, in DMF): 158 (2:1). Color: white.

[AgL⁴](ClO₄)·4H₂O (8). Anal. Calcd for $C_{32}H_{50}N_{10}ClO_8Ag$ (MW 846.1): C, 45.4; H, 5.9; N, 16.6. Found: C, 45.5; H, 5.7; N, 16.8. Yield: 55%. IR (KBr, cm⁻¹): 1600, 1575, 1470, 1463 (ν-(C=N)$_{py}$ and ν(C=C)), 2245 (ν(C≡N)), 1100, 626 (ν(ClO₄⁻)). MS (L-SIMS, m/z): 673 amu [AgL⁴]⁺. Λ_M (Ω^{-1} cm² mol⁻¹, in DMF): 80 (1:1). Color: white.

[Ag₂L⁴](ClO₄)₂ (9). Anal. Calcd for $C_{32}H_{42}N_{10}Cl_2O_8Ag_2$ (MW 978.1): C, 39.2; H, 4.3; N, 14.3. Found: C, 39.0; H, 4.3; N, 14.4. Yield: 30%. IR (KBr, cm⁻¹): 1596, 1578, 1459, 1448 (ν(C=N)$_{py}$ and ν(C=C)), 2250 (ν(C≡N)), 1100, 625 (ν(ClO₄⁻)). MS (L-SIMS, m/z): 881 [Ag₂L⁴(ClO₄)]⁺, 673 amu [AgL⁴]⁺. Λ_M (Ω^{-1} cm² mol⁻¹, in DMF): 180 (2:1). Color: white.

X-ray Crystallography. Crystals were obtained by slow recrystallization from acetonitrile in all cases. The details of the X-ray crystal data and the structure solution and refinement are given in Table 2. Measurements were made on a Bruker SMART CCD area diffractometer with graphite-monochromated Mo Kα radiation. All data were corrected for Lorentz and polarization effects. Empirical absorption corrections were also applied.[33] Complex scattering factors were taken from the program package SHELXTL.[34] The structures were solved by direct methods, which revealed the position of all non-hydrogen atoms. All the structures were refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms were located in their calculated positions and refined using a riding model.

Supporting Information Available: CIF data (cif), fluorescence emission spectra in solid state for **2** and **4**, ¹H NMR titration curves for the addition of perchlorate silver(I) salt, and ¹H NMR spectra for L² and L³ (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

IC051627R

(33) Sheldrick, G. M. *Sadabs, Program for empirical absorption correction of area detector data*; University of Göttingen, Göttingen, Germany, 1996.

(34) SHELXTL version, *An integrated system for solving and refining crystal structures from diffraction data (Revision 5.1), Bruker AXS LTD.*