

## Polymer Building Blocks: Self-Assembly of Silver(I) Cyclotriphosphazene Cationic Columns

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The multimodal ligand hexakis(2-pyridyloxy)cyclotriphosphazene (L) and its 4-methyl-2-pyridyloxy analogue (MeL) react with Ag(I) to afford  $\{[AgL]^+\}_\infty$  supramolecular cationic columns via self-assembly, with the anions occupying the intercolumnar channels. In contrast, the reaction of MeL with Cu(I) yields a dimetallic Cu(II) complex containing  $\mu$ -OH and  $\mu$ -4-methyl-2-pyridyloxy bridges.

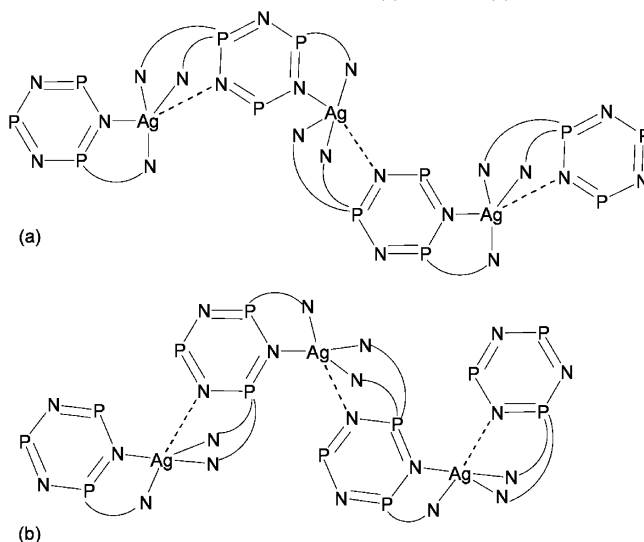
The design of new coordination polymers is a topical and rapidly expanding area because of the applications potentially offered by these materials and the degree of synthetic control available for their fine-tuning.<sup>1</sup> Silver(I) is the metal component frequently chosen in these systems, and the topologies observed with nitrogen-based heterocycles are diverse.<sup>2</sup> Ligand design is a key issue in controlling topology, and recently the nature of multimodal ligand binding in this role has been addressed.<sup>3</sup>

Virtually unexplored is the use of substituted cyclophosphazene rings as scaffolds for the construction of supramolecular metallopolymers by self-assembly, and yet they offer an appealing and accessible class of multimodal ligands for this purpose. Hexakis(2-pyridyloxy)cyclotriphosphazene (L), and its 4-methyl-2-pyridyloxy analogue (MeL), is a multimodal ligand that has the capability of binding to metal ions via both the phosphazene ring nitrogen and pendant pyridyloxy nitrogen atoms.

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Chart 1. Section of the Cationic Chains (a) in **1** and (b) in **3**



As part of our program to examine the coordination chemistry of polyphosphazene-based ligands, we have previously described copper(II) complexes of L and its 4-methyl-2-pyridyloxy analogue, MeL, demonstrating that they are versatile multimodal ligands with the capability of binding to metal ions in mono-, tri-, and pentadentate modes.<sup>4</sup> A key feature of the design of the ligands is the incorporation of flexible pyridyloxy pendant arms, which enhance metal-ion binding to the phosphazene ring nitrogen, as well as provide key linking groups. This is illustrated in this paper, which reports the first examples of the self-assembly of supramolecular metallopolymers using cyclophosphazene building blocks in which both the ring nitrogen atoms and pendant donor atoms bind directly to the metal atoms (Chart 1). The resulting structures contain supramolecular cationic columns, which enclose the silver(I) ions, leaving the co-anions to occupy the intercolumnar channels. The only other report of crystallographically characterized coordination polymers involving cyclotriphosphazene linkages is that of Richards

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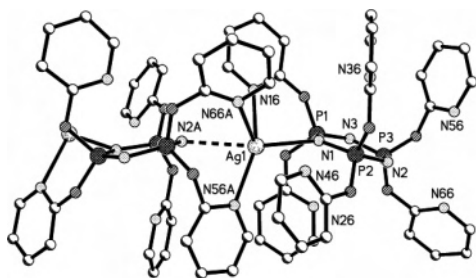


Figure 1. Section of the cation in **1**.

and Steiner,<sup>5</sup> who reported the structures of several silver(I) coordination polymers of hexakis(alkylamino)cyclotriphosphazenes. In these examples, coordination of the ring nitrogen atoms to two or three silver ions results in 2D sheets or 1D chains. However, in contrast to the results with **L** and **MeL**, the pendant NH groups do not interact with the Ag atoms, but instead hydrogen bonding between them and the anions ( $\text{ClO}_4^-$  and  $\text{NO}_3^-$ ) plays a critical role in stabilizing the overall structures in the solid state.

A dichloromethane solution containing **L** and  $[\text{Ag}(\text{MeCN})_4]\text{PF}_6$  in a 1:1 molar ratio afforded a white powder upon precipitation with hexane. Vapor diffusion of diethyl ether into an acetonitrile solution of this precipitate produced crystals of  $\{[\text{AgL}]\text{PF}_6\}_\infty$  (**1**). Figure 1 shows how the silver cations in **1** are coordinated by pyridine and phosphazene ring nitrogen donors from adjacent phosphazene rings. The silver ions are in a highly irregular five-coordinate geometry. The Ag–N bond lengths lie between 2.347(2) and 2.595(2) Å for the four closest donors, and the N–Ag–N angles vary between 78.62(5) and 150.26(6)°. The silver ion forms a bond of length of 2.464(2) Å to N1 of the phosphazene ring that contributes one pyridyloxy nitrogen to the donor set and a longer bond of 2.798(2) Å to N2A of the adjacent phosphazene ring, which contributes a further two *gem*-pyridyloxy nitrogen donors.

Suitable crystals for X-ray studies were not obtained for the MeL analogue of **1**, viz.,  $\{[\text{Ag}(\text{MeL})]\text{PF}_6\}_\infty$  (**2**); however, crystals of  $\{[\text{Ag}(\text{MeL})]\text{NO}_3\}_\infty$  (**3**) were grown by layering a dichloromethane solution of MeL with a methanol solution of  $\text{AgNO}_3$  and allowing the solutions to diffuse. Again the geometry about the five-coordinate Ag(I) centers in **3** (Figure 2) is irregular and in this case is best described as distorted trigonal-bipyramidal ( $\tau = 0.54$ ).<sup>6</sup> There are two sets of Ag–N contacts: four shorter bonds [2.293(4)–2.482(4) Å] and one longer one to N2A of 2.768(3) Å. The axial angle between the coordinating phosphazene ring nitrogen atom N2 and the pyridyl nitrogen atom N16A from an adjacent phosphazene ring is 162.1(1)°. Angles between pyridyloxy donors and the phosphazene ring nitrogen in the equatorial plane are between 110.2(1) and 129.4(1)°.

In both **1** and **3**, the ligand donor sets are the same, and the overall topology is that of a 1D polymeric chain. The structures differ subtly in that the silver coordination spheres are not made from conformationally equivalent donors. In

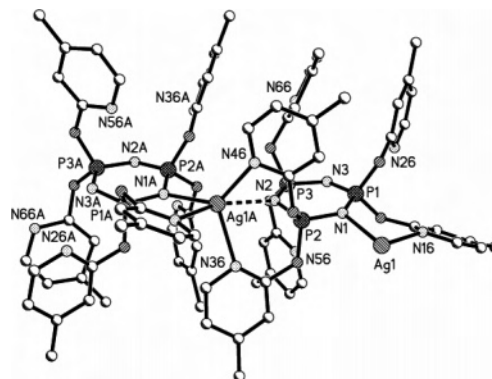


Figure 2. Section of the cation in **3**.

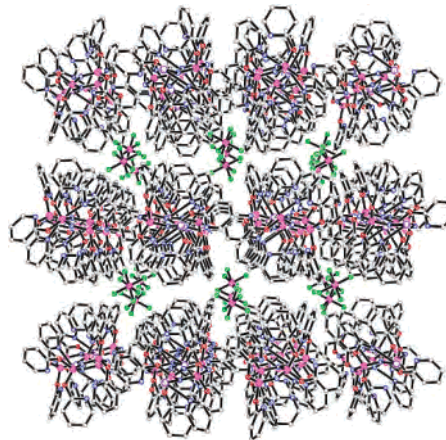


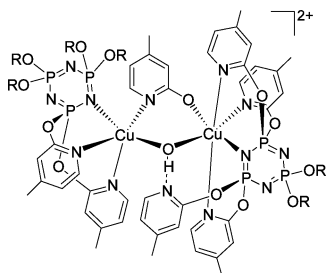
Figure 3. End-on view of **1** showing the cationic chains and the channels containing the  $\text{PF}_6^-$  anions.

**1**, two of the pyridyloxy donors approach from one side of the chain and the third donor approaches from the opposite side (Chart 1a). In **3**, all three pyridyloxy arms approach from the same side of the chain (Chart 1b). The overall effect is that in **3** the chains are wider and more compressed. For example, the closest  $\text{Ag}\cdots\text{Ag}$  distance in **3** at 6.224 Å is approximately 1.5 Å less than that in **1**, and the adjacent Ag atom in the chain is approximately 4.5 Å closer. To accommodate three pyridyloxy donors on the same side of the chain, the phosphazene links in **3** zigzag more acutely than in **1**; the  $\text{N}_{\text{phosphazene}}-\text{Ag}-\text{N}_{\text{phosphazene}}$  angle in **3** is 113.9(1)°, whereas in **1**, the equivalent angle is 153.4(5)°. The phosphazene rings are not significantly distorted from planarity in either structure: the maximum deviations from the mean  $\text{N}_3\text{P}_3$  planes are ca. 0.073 Å for N3 in **1** and 0.053 Å for P2 in **3**.

In both structures, the ordering in the lattice is similar. Parallel cationic columns are arranged side by side in sheets, with the anions lying in channels above and below each sheet (e.g., Figure 3). Adjacent parallel chains are then able to interlink through stacking interactions of the pyridyl rings. Thus, in **1**, the centroid of pyridyloxy ring 4 lies approximately 3.53 Å from the centroid of the symmetrically equivalent ring on the adjacent chain. Pyridyloxy ring 5 from the next phosphazene link in the polymer and its symmetry equivalent on the adjacent chain form stacks on either side of the interlinking rings. This four-ring stacking array both bridges adjacent chains and links adjacent polymer units. In

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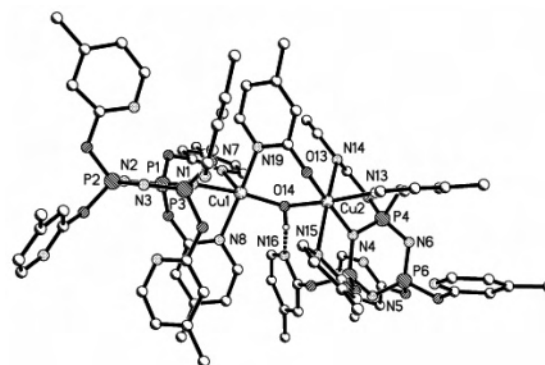
**Chart 2.**  $[\text{Cu}_2(\text{MeL})_2(\mu\text{-OH})(\mu\text{-4-MeOpy})](\text{PF}_6)_2$  ( $\text{R} = 4\text{-Mepy}$ ) (**5**)

**3**, interstrand  $\pi$  interactions occur between ring 1 and its coplanar symmetry equivalent. The distance  $\text{C13}\cdots\text{C13}'$  is ca. 3.535 Å in the offset face-to-face stack. Interlink interactions occur between the nearly coplanar pyridyloxy rings 4 and 5 of adjacent phosphazenes; the atoms C43 and C52' in these rings are ca. 3.413 Å apart.

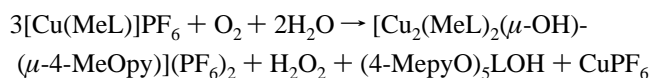
In both polymers, the silver ions are deprived of any weak coordination to the anions because these are buried within the network of pyridyloxy rings, with the closest  $\text{Ag}-\text{P}_{\text{hexafluorophosphate}}$  distance being 7.822 Å in **1** and the closest  $\text{Ag}-\text{N}_{\text{nitrate}}$  distance being ca. 6.7 Å in **3**. However, hydrogen-bonding interactions are present between the hydrogen atoms of the pyridyloxy rings and the fluorine atoms in **1** or nitrate oxygen atoms in **3**. This hydrogen-bonding network has the effect of bridging the chains in a direction perpendicular to the  $\pi$ -stacking interactions described above. The atomic positions of the fluorine atoms in **1** are well-defined but, in contrast, the nitrate ion in **3** is disordered within its site.

The  $^{31}\text{P}$  NMR spectra of **1** and **3** in  $\text{CD}_3\text{CN}$  show singlets (at  $\delta$  6.91 and 6.89 ppm, respectively), and the  $^1\text{H}$  NMR spectra show only one set of ligand peaks, implying that in solution the polymeric structure is lost or the ligand arms are exchanging rapidly. While there is a precedent for fluxional solution behavior of  $d^{10}$  ions with hexakis-substituted cyclotriphosphazenes<sup>7</sup> and  $\text{Ag}(\text{I})$  ions in complexes of hexakis(pyrazolyl-1-yl)benzene also exhibit intramolecular shifting in solution,<sup>8</sup> these are not polymeric complexes. The fact that the electrospray mass spectra using acetonitrile as the solvent show only ions at  $m/z$  values corresponding to the monomeric cations, viz.,  $[\text{AgL}]^+$  for **1** and  $[\text{Ag}(\text{MeL})]^+$  for **2**, suggests that the polymers dissociate in solution. The cyclotriphosphazene P–N ring stretching frequencies show only small shifts in **1** and **2** compared with free ligand values, which is consistent with the observation that silver coordination to the phosphazene ring nitrogen has not caused them to distort significantly from planarity. For example, bands at 1222 and 1184  $\text{cm}^{-1}$  for **L** are observed at 1223, 1204, and 1184  $\text{cm}^{-1}$  for **1**.

The reactions between  $\text{Cu}(\text{I})$  and **L** or **MeL** were complicated by their subsequent solution redox chemistry. A white

**Figure 4.** Structure of **5**.

powder from the reaction between  $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$  and **L** gave microanalytical data consistent with the formulation  $[\text{CuL}]\text{PF}_6$  (**4**), and IR data were comparable with those of **1**. The corresponding reaction of **MeL** with  $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$  initially gave a colorless oil, but green crystals were obtained in low yield when this was dissolved in an acetonitrile/ether solution. Single-crystal X-ray data show the structure to be  $[\text{Cu}_2(\text{MeL})_2(\mu\text{-OH})(\mu\text{-4-MepyO})](\text{PF}_6)_2$  (**5**; 4-MepyO is the 4-methyl-2-pyridyloxy anion; Chart 2 and Figure 4). The  $\mu\text{-4-MeOpy}$  and  $\mu\text{-OH}$  bridges give rise to an unusual dimetallic complex with inequivalent  $\text{Cu}(\text{II})$  centers 3.404 Å apart.  $\text{Cu1}$  is in an approximate square-based pyramidal coordination sphere with an “ $\text{N}_4\text{O}$ ” donor set,<sup>9</sup> whereas  $\text{Cu2}$  is in a distorted “ $\text{N}_4\text{O}_2$ ” rhombic environment.<sup>10</sup> The hydroxo bridge participates in an intramolecular hydrogen bond with  $\text{N16}$  of a pyridyloxy arm, and its oxygen atom  $\text{O14}$  also forms a close contact (ca. 3.03 Å) with  $\text{N14}$  of another. The formation of **5** could be envisaged to occur according to the following equation, although we have not detected hydrogen peroxide because it would be expected to react with any  $\text{Cu}(\text{I})$  species formed.



Although these observations with  $\text{Cu}(\text{I})$  are cursory, they highlight the differences in behavior between the  $\text{Ag}(\text{I})$  and  $\text{Cu}(\text{I})$  complexes of **L** and **MeL**.

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**Supporting Information Available:** Experimental details (PDF) along with crystallographic data for **1**, **3**, and **5** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(9) Bond lengths (Å): basal  $\text{Cu1}-\text{O14}$  1.900(5),  $\text{Cu1}-\text{N19}$  2.014(7),  $\text{Cu1}-\text{N1}$  2.046(7),  $\text{Cu1}-\text{N8}$  2.069(7); axial  $\text{Cu1}-\text{N7}$  2.343(6).

(10) Bond lengths (Å): equatorial  $\text{Cu2}-\text{O14}$  1.908(5),  $\text{Cu2}-\text{O13}$  1.948(6),  $\text{Cu2}-\text{N13}$  2.052(7),  $\text{Cu2}-\text{N4}$  2.067(7); axial  $\text{Cu2}-\text{N14}$  2.670(7),  $\text{Cu2}-\text{N15}$  2.541(7).