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Article

Cyclophosphazenes as Nodal Ligands in Coordination Polymers

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Herein, we show that cyclotriphosphazenes carrying organo amino side chains, $(RNH)_6P_3N_3$ {R = *n*-propyl (**1**), cyclohexyl (**2**), benzyl (**3**)}, and $(C_4H_8N)_6P_3N_3$ (**4**) produce supramolecular coordination compounds in conjunction with silver salts by formation of linear N–Ag–N connections via nitrogen centers of the phosphazene ring. Crystalline materials were obtained by layering methanol solutions containing phosphazene ligands with methanol solutions of $AgClO_4$ and $AgNO_3$. The donor ability of the anion and the steric demand of the lipophilic ligand sphere R control the topology of the coordination network: $(\mathbf{1})_2(AgClO_4)_3$ forms a graphite-type (6,3) network. All three N(ring) atoms of the phosphazene ligand coordinate to silver ions, which, in return, linearly bridge two phosphazene ligands. The phosphazene–Ag(I) arrangement in $\mathbf{1}(AgNO_3)_2$ exists of zigzag chains featuring one bridging silver ion and one terminally coordinated silver ion per ligand molecule. The terminally located Ag(I) ions of neighboring chains are bridged by nitrate ions, resulting in a 2D network. Both $\mathbf{2}(AgClO_4)$ and $\mathbf{4}(AgClO_4)$ contain only one bridging silver ion per phosphazene ligand, which leaves one N(ring) site vacant and gives 1D zigzag chain arrangements. The crystal structures of $\mathbf{3}(AgClO_4)_2$ and $\mathbf{3}(AgNO_3)_2$ resemble that of $\mathbf{1}(AgNO_3)_2$, but show additional Ag–π(aryl) interactions between the terminally arranged silver ions and benzyl groups. Treatment of **3** with a methanol solution containing both $AgNO_3$ and $AgClO_4$ leads to the heteroanion derivative $\mathbf{3}(AgNO_3)(AgClO_4)$. Phosphazene ligands **1**–**3** have the ability to undergo hydrogen bonding to anions via the six NH groups, and the coordination polymers containing these ligands feature dense networks of NH···O bonds.

Introduction

Organo nitrogen heterocycles have been widely employed as bridging ligands in coordination polymers, since the stereorigid arrangement of N-donor sites provides great control over the topology of the supramolecular network.[1] Conversely, coordination polymers containing inorganic N-heterocycles are scarce.[2] This seems surprising, since many inorganic N-heterocyclic ligands offer arrays of multiple N-donor sites and display a rich coordination chemistry.[3] Cyclotriphosphazenes are prominent examples of inorganic N-heterocycles. They consist of six-membered ring structures of alternating phosphorus and nitrogen atoms. The tetravalent phosphorus atoms carry two exocyclic substituents, which can be widely varied, enabling fine-tuning of the size and shape of the molecular periphery and allowing provision of additional donor sites.[4] Cyclophosphazenes show a versatile coordination behavior, particularly in the form of multidentate ligands carrying additional exocyclic donor functions.[5] The donor topology of the cyclotriphosphazene ring is equivalent to that of 1,3,5-triazines, but the tetrahedral environment of the P(ring) atoms places the exocyclic substituents above and below the phosphazene ring plane, which provides ample space for metal coordination to N(ring) sites. The potential of cyclophosphazenes to form M−L−M

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(1) (a) Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2638. (b) Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W.-S.; Withersby, M. A.; Schröder, M. *Coord. Chem. Rev.* **1999**, *183*, 117. (c) Khlobystov, A. N.; Blake, A. J.; Champness, N. R.; Lemenovskii, D. A.; Majouga, A. G.; Zyk, N. V.; Schröder, M. *Coord. Chem. Rev.* **2001**, *222*, 155. (d) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629. (e) Kaim, W. *Coord. Chem. Rev.* **2002**, *230*, 127. (f) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (g) Swiegers, G. F.; Malefetse, T. J. *Chem. Rev.* **2000**, *100*, 3483. (h) Carlucci, L.; Ciani, G.; Prosperio, D. M.; Porta, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 317.

(2) For a rare example see: Thewalt, U.; Müller, B. *Z. Anorg. Allg. Chem.* **1980**, *462*, 218.

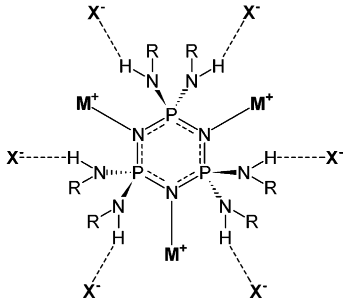
(3) (a) Stahl, L. *Coord. Chem. Rev.* **2000**, *210*, 203. (b) Chivers, T.; Hilts, R. W. *Coord. Chem. Rev.* **1994**, *137*, 201. (c) Witt, M.; Roesky, H. W. *Chem. Rev.* **1994**, *94*, 1163. (d) Allcock, H. R.; Desorcie, J. L.; Riding, G. H. *Polyhedron* **1987**, *6*, 119.

(4) (a) Allcock, H. R. *Chem. Rev.* **1972**, *72*, 315. (b) Chandrasekhar, V.; Krishnan, V. *Adv. Inorg. Chem.* **2002**, *53*, 159. (c) Allen, C. W. *Chem. Rev.* **1991**, *91*, 119.

(5) (a) Steiner, A.; Zacchini, S.; Richards, P. I. *Coord. Chem. Rev.* **2002**, *227*, 193. (b) Chandrasekhar, V.; Nagendran, S. *Chem. Soc. Rev.* **2001**, *30*, 192.

10.1021/ic035455e CCC: $27.50

Scheme 1. Potential Binding Sites for Metal Cations (M^+) and Anions ($X-$) around the Phosphazene Ligand $(RNH)_6P_3N_3$



or L−M−L bridges, where L represents the cyclophosphazene ligand and M a metal center, has been demonstrated in a number of cases, all of which, however, are confined to molecular complexes.[6,7] Structurally characterized coordination polymers containing cyclophosphazenes have not been reported so far.

Herein, we show that cyclotriphosphazenes can serve as stereorigid bridging ligands in the presence of silver salts, contrasting the variable networking behavior of the related 1,3,5-triazine ligand.[8] The basicity of the ring nitrogen atoms in phosphazenes is correlated to the electronic properties of the exocyclic substituent at phosphorus. To enhance the donor ability of N(ring) atoms, we have utilized phosphazene ligands with primary and secondary organo amino substituents that include $(RNH)_6P_3N_3$ {R = *n*-propyl (**1**), cyclohexyl (**2**), benzyl (**3**)}[9] and $(C_4H_8N)_6P_3N_3$ (**4**).[10] Phosphazene ligands **1**−**3** carry six NH groups, which are able to interact with anions via hydrogen bonding (Scheme 1). Hence, in the presence of oxo anions ClO_4^- and NO_3^- the formation of a dense network of NH···O interactions is anticipated. In addition, the freedom of rotation around the six exocyclic P−N bonds permits effective interlocking of R groups of neighboring ligand molecules and provides flexible coordination modes for hydrogen bonding, due to the variable directionality of NH bonds.[9] Furthermore, ligand **3** features six aryl groups offering weak binding sites for silver ions, which promises a hemilabile ligand behavior.

Results and Discussion

The addition of a methanol solution containing phosphazene ligands **1**−**4** to a methanol solution containing either silver perchlorate or silver nitrate gives amorphous precipitates. Careful layering of both solutions containing the phosphazene and the silver salt in a 1:3 ratio leads to the formation of single crystals, which grow from the interface of the two liquid phases. X-ray structure analyses and microanalyses reveal the formation of metal complexes of compositions $(\mathbf{1})_2(AgClO_4)_3$, $\mathbf{1}(AgNO_3)_2$, $\mathbf{2}(AgClO_4)$, $\mathbf{3}(AgClO_4)_2$, $\mathbf{3}(AgNO_3)_2$, and $\mathbf{4}(AgClO_4)$. The IR spectra exhibit a red shift of about 20 cm^{-1} of the stretching frequencies of phosphazene rings compared to corresponding IR frequencies of the free ligands, indicating the coordination of N(ring) atoms to silver ions. The nitrate derivatives are of high thermal stability. The thermogravimetric analysis of $\mathbf{3}(AgNO_3)_2$ shows no weight loss up to 210 °C. Also, the crystalline material of $\mathbf{3}(AgNO_3)_2$ is not degraded by prolonged treatment with refluxing toluene.

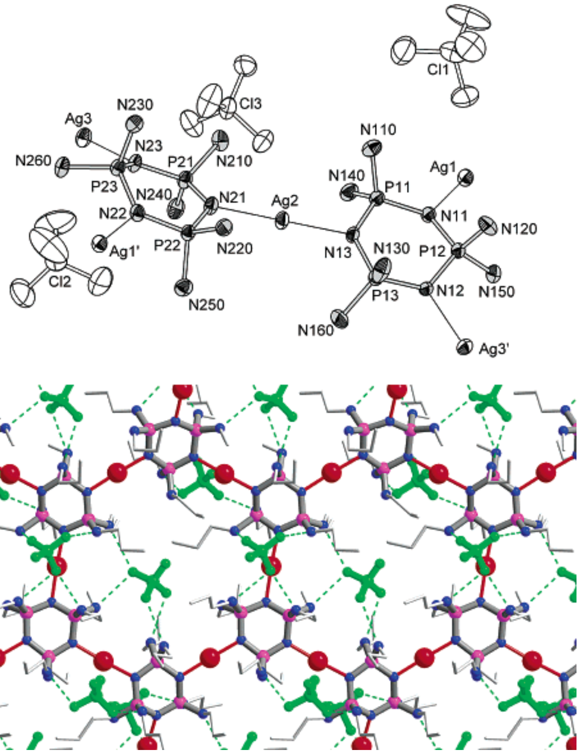


Figure 1. Crystal structure of $(\mathbf{1})_2(AgClO_4)_3$. Top: asymmetric unit, 50% ellipsoids; C and H atoms are omitted. Bottom: supramolecular structure; Ag, red; N, blue; P, purple; R, light gray; ClO_4^-, green; H atoms are omitted.

The crystal structure of the *n*-propyl derivative $(\mathbf{1})_2(AgClO_4)_3$ comprises a graphite-type (6,3) network (Figure 1). The phosphazene ligand acts as a trigonal planar node binding three silver ions, which in turn are linearly coordinated by phosphazene ligands. The perchlorate ions do not coordinate to silver ions in the solid state, but form hydrogen bonds with NH groups of the phosphazene ligands. The layers of inorganic frameworks comprising Ag, P, and N are stacked in almost eclipsed fashion, forming hexagonal channels orthogonal to the layers, which are filled with propyl groups of the ligands and one of the three unique perchlorate ions. The shortest distance between silver ions across the channel measures 12.2 Å. The crystal structure contains two crystallographically independent phosphazene ligands bearing distinctive conformations of both phosphazene rings (*chair* and *boat*) and exocyclic NHR groups. The ligand molecules contribute six and four NH groups, respectively, to H bonding

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(6) For M−L−M bridges see: (a) Byun, Y.; Min, D.; Do, J.; Yun, H.; Do, *Inorg. Chem.* **1996**, *35*, 3981. (b) Min, D.; Do, Y. *Chem. Lett.* **1994**, 1989.

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(8) (a) Venkataraman, D.; Lee, S.; Moore, J. S.; Zhang, P.; Hirsch, K. A.; Gardner, G. B.; Covey, A. C.; Prentice, C. L. *Chem. Mater.* **1996**, *8*, 2030. (b) Bertelli, M.; Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Mater. Chem.* **1997**, *7*, 1271. (c) Blake, A. J.; Brooks, N. R.; Champness, N. R.; Cooke, P. A.; Deveson, A. M.; Fenske, D.; Hubberstey, P.; Li, W.-S.; Schröder, M. *Dalton Trans.* **1999**, 2103.

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(10) (a) Kropatschawa, K. *Zh. Obshch. Khim.* **1965**, *35*, 1988 (b) Butour, J.-L.; Labarre, F. Sournies, J.-F. *J. Mol. Struct.* **1980**, *65*, 51.

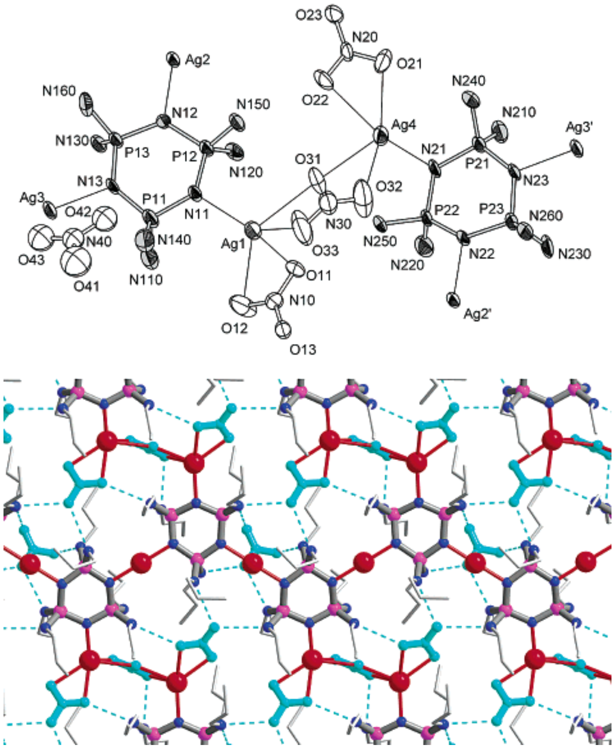

Figure 2. Crystal structure of **1**$(AgNO_3)_2$. Top: asymmetric unit, 50% ellipsoids; C and H atoms are omitted. Bottom: supramolecular structure; Ag, red; N, blue; P, purple; R, light gray; NO_3^-, turquoise; H atoms are omitted.

to perchlorate ions. Owing to the variable directionality of the twelve crystallographically unique NH bonds, the three unique perchlorate ions encounter distinct coordination modes: As mentioned above, one is accommodated in the channels of the inorganic framework and forms three H bonds with two ligands. The other two ClO_4^- ions are situated between the layers, each interacting with two ligands of one layer, one via two and the other via four hydrogen bonds.

In the silver nitrate complex **1**$(AgNO_3)_2$, phosphazene molecules and silver ions form zigzag chains, which are interlinked by nitrate ions, forming a 2D sheet structure (Figure 2). Again, all three N(ring) atoms of the ligand are involved in metal coordination. Two N(ring) atoms bind to linearly bridging silver ions, while the third N(ring) atom coordinates a silver ion, which is part of a $(AgNO_3)_2(\mu\text{-}NO_3)$ arrangement that forms a bridge to the neighboring chain. The differences in network structure and stoichiometry between (**1**)$_2(AgClO_4)_3$ and **1**$(AgNO_3)_2$ are due to the stronger donor ability of the nitrate ion over the perchlorate ion. The 2D sheet structure of **1**$(AgNO_3)_2$ is formally obtained by inserting $AgNO_3$ into one set of parallel N−Ag−N connections of the (6,3) network comprising phosphazene ligands and silver ions of (**1**)$_2(AgClO_4)_3$. In addition to silver coordination, nitrate ions form a dense network of NH···O bonds with ligand molecules in **1**$(AgNO_3)_2$ involving six NH groups of one and five NH groups of the other crystallographically unique phosphazene ligand. The four crystallographically unique nitrate ions in **1**$(AgNO_3)_2$ fall into three categories: One forms four hydrogen bonds, the second chelates two silver ions, and the remaining two are involved in both H bonding and coordination to one Ag ion.

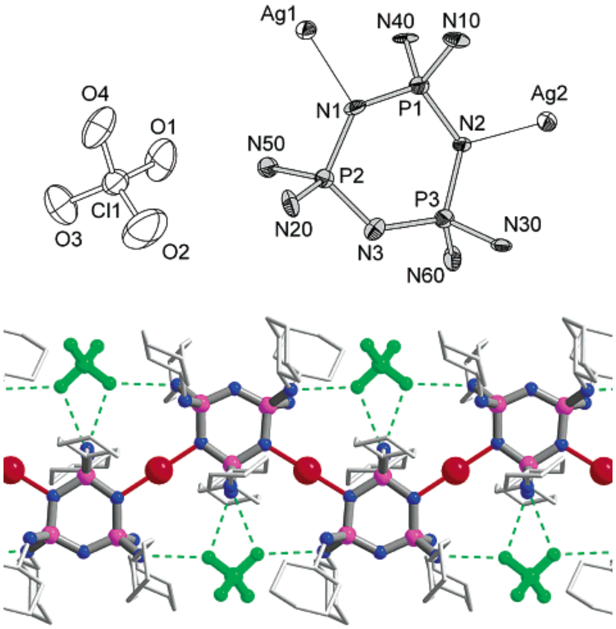

Figure 3. Crystal structure of **2**$(AgClO_4)$. Top: asymmetric unit, 50% ellipsoids; C and H atoms are omitted. Bottom: supramolecular structure; Ag, red; N, blue; P, purple; R, light gray; ClO_4^-, green; H atoms are omitted.

The crystal structure of **2**$(AgClO_4)$ exists as a one-dimensional coordination polymer (Figure 3). The presence of the bulkier cyclohexyl group in the ligand periphery of **2** reduces the number of ring nitrogen atoms coordinating to metal ions. Two nitrogen atoms of the phosphazene ring coordinate silver ions, which in turn are linearly coordinated by phosphazene ligands, resulting in the formation of zigzag chains. Perchlorate ions are accommodated within the chain structure via NH···O interactions with ligand molecules. Four NH groups per ligand interact with two O atoms of perchlorate ions.

The coordination polymers **3**$(AgClO_4)_2$ (Figure 4) and **3**$(AgNO_3)_2$ (Figure 5) show zigzag chain arrangements containing bridging and terminally arranged silver ions, which resemble the core structure of Ag, P, and N atoms in **1**$(AgNO_3)_2$. In addition, aryl groups of the ligand molecules participate in the coordination of terminally arranged silver ions. Two benzyl groups undergo Ag−C contacts in **3**$(AgClO_4)_2$: One benzyl group coordinates in an asymmetrical η^2-fashion, displaying Ag−C distances of 2.531(4) and 2.663(4) Å. The other benzyl group is η^1-coordinated, showing a Ag−C contact of 2.572 Å. In the corresponding nitrate derivative **3**$(AgNO_3)_2$ one benzyl group is η^1-coordinated to the terminal Ag ion (Ag−C = 2.524(4) Å). The Ag−C distances discussed here are in agreement with reported Ag−π(aryl) distances.[11] The lesser involvement of aryl groups in the metal coordination of **3**$(AgNO_3)_2$ reflects the stronger donor ability of the nitrate ion, which also coordinates the silver ion in a bidentate fashion, contrasting

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(11) Munakata, M.; Wu, L. P.; Ning, G. L. *Coord. Chem. Rev.* **2000**, *198*, 171 and references therein.

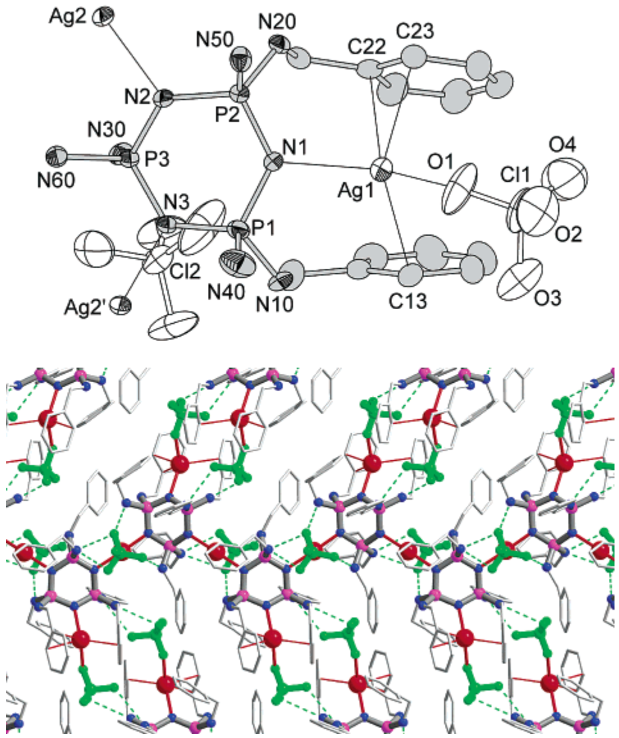

Figure 4. Crystal structure of **3**$(AgClO_4)_2$. Top: asymmetric unit, 50% ellipsoids; only C atoms of coordinating benzyl groups are shown. Bottom: supramolecular structure; Ag, red; N, blue; P, purple; R, light gray; ClO_4^-, green; H atoms are omitted.

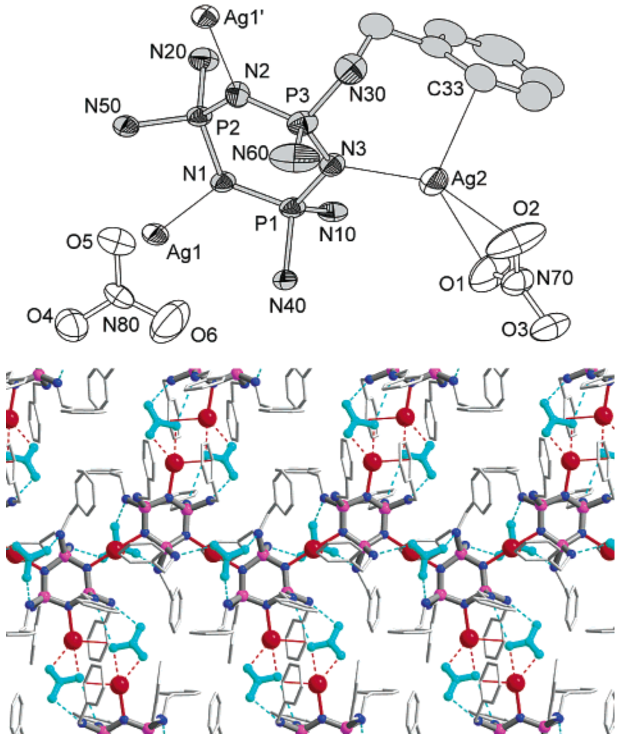

Figure 5. Crystal structure of **3**$(AgNO_3)_2$. Top: asymmetric unit, 50% ellipsoids; only C atoms of coordinating benzyl groups are shown. Bottom: supramolecular structure; Ag, red; N, blue; P, purple; R, light gray; NO_3^-, turquoise; H atoms are omitted.

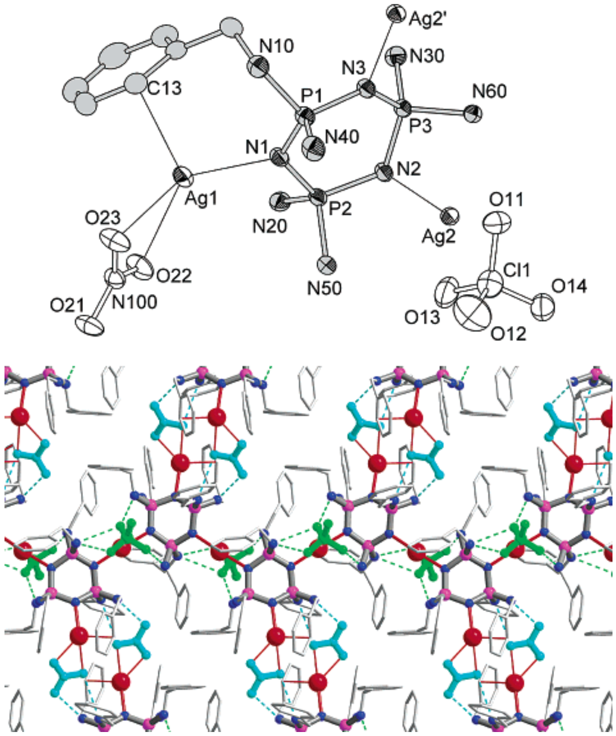

Figure 6. Crystal structure of **3**$(AgClO_4)(AgNO_3)$. Top: asymmetric unit, 50% ellipsoids; only C atoms of coordinating benzyl groups are shown. Bottom: supramolecular structure; Ag, red; N, blue; P, purple; R, light gray; NO_3^-, turquoise; ClO_4^-, green; H atoms are omitted.

the monodentate interaction of perchlorate ions in **3**$(AgClO_4)_2$. There are two crystallographically distinct anion sites in **3**$(AgClO_4)_2$ and **3**$(AgNO_3)_2$: One anion is coordinated to the metal ion and, in addition, forms a link to the neighboring polymer chain by N−H···O contacts, while the other anion is not involved in metal ion coordination, but interacts solely by hydrogen bonding with two ligands of the same coordination polymer.

The presence of two distinct anion sites in **3**$(AgClO_4)_2$ and **3**$(AgNO_3)_2$ tempted us to prove the anion binding selectivity of the coordination polymer by treating **3** with a mixture of $AgNO_3$ and $AgClO_4$. Crystals of the heteroanion derivative **3**$(AgClO_4)(AgNO_3)$ were obtained by layering a solution of the phosphazene ligand in methanol with a methanol solution containing both $AgClO_4$ and $AgNO_3$. The crystal structure shows a coordination network (Figure 6), which is equivalent to those of **3**$(AgClO_4)_2$ and **3**$(AgNO_3)_2$. In the heteroanion complex the nitrate ions occupy the metal-coordinated site, while perchlorate ions are located in the hydrogen-bonded site. Hence, in accordance with their donor ability, the two anions are distributed selectively over the two distinct sites. Similar to the coordination mode of the terminal silver ion in **3**$(AgNO_3)_2$, one benzyl group of the ligand is η^1-coordinated to the silver ion in the mixed-anion derivative, displaying a Ag−C contact of 2.476(3) Å. Apart from their anionic moieties, the crystals of **3**$(AgClO_4)_2$, **3**$(AgNO_3)_2$, and **3**$(AgClO_4)(AgNO_3)$ are nearly isostructural. All three structures adopt the same space group and show very similar unit cell parameters. Besides, a comparison of ligand conformations (Figure 7) reveals a close resemblance: The orientations of benzyl groups in **3**$(AgNO_3)_2$ and **3**$(AgClO_4)(AgNO_3)$ are more or less identical, and those of **3**$(AgClO_4)_2$ show only slight deviations from both former ones. This is due to the additional coordination of the second benzyl group, which bends away from the silver ion in the

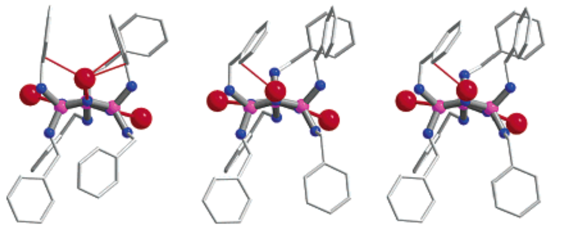

Figure 7. Comparison of ligand conformations of **3**($AgClO_4$)$_2$ (left), **3**($AgNO_3$)$_2$ (middle), and **3**($AgClO_4$)($AgNO_3$) (right).

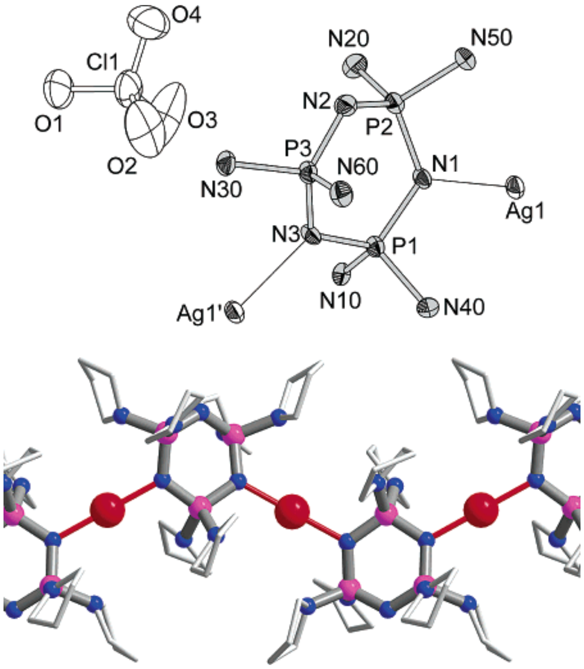

Figure 8. Crystal structure of **4**($AgClO_4$). Top: asymmetric unit, 50% ellipsoids; C and H atoms are omitted. Bottom: supramolecular structure; Ag, red; N, blue; P, purple; R, light gray; ClO_4^-, green; H atoms and ClO_4^- ions are omitted.

presence of the more strongly binding nitrate ions, demonstrating the hemilabile character of the ligand.

The solid-state structure of **4**($AgClO_4$) exhibits a zigzag chain arrangement comprised of Ag^+ ions and phosphazene ligands, which corresponds to that of **2**($AgClO_4$) (Figure 8). There are, however, no direct contacts between the coordination polymer and the perchlorate ions, due to the absence of H-donor functions in **4**. This indicates that hydrogen bonding between ligands and perchlorate ions plays a far less governing role than Ag−N interactions in the supramolecular assembly of (**1**)$_2$($AgClO_4$)$_3$ and **2**($AgClO_4$). In effect, the steric demand of the bulky substituents determines the supramolecular structure in both compounds by limiting the number of silver ions coordinating to the phosphazene ring. It should be noted, however, that perchlorate ions in (**1**)$_2$($AgClO_4$)$_3$, **2**($AgClO_4$), and **3**($AgClO_4$)$_2$ show no crystallographic disorder, since they are fixed in their positions by H bonds, whereas the disorder of the perchlorate ion in **4**($AgClO_4$) suggests unhindered rotation of the ion in the crystal lattice.

The Ag−N distances involving bridging silver ions of all structures presented here range from 2.104(9) to 2.164(3) Å. The Ag−N distances of the terminally arranged silver ions in **1**($AgNO_3$)$_2$, **3**($AgClO_4$)$_2$, **3**($AgNO_3$)$_2$, and **3**($AgClO_4$)($AgNO_3$) are somewhat longer, ranging from 2.217(9) to 2.260(2) Å. The P−N(ring) bonds (av 1.62 Å) and exocyclic P−N bonds (av 1.62 Å) are of equal lengths in phosphazene rings coordinating silver ions via all three N(ring) atoms, which include complexes (**1**)$_2$($AgClO_4$)$_3$, **1**($AgNO_3$)$_2$, **3**($AgClO_4$)$_2$, **3**($AgNO_3$)$_2$, and **3**($AgClO_4$)($AgNO_3$). This contrasts the bonding parameters of the free ligands **1**−**3**, which have shorter P−N(ring) bonds (av 1.60 Å) and longer exocyclic P−N bonds (av 1.66 Å),[9] and shows the impact of metal coordination on the P_3N_9 core structure of the ligand. In **2**($AgClO_4$) and **4**($AgClO_4$), the phosphazene ring contains one noncoordinating N center. The P−N(ring) bonds at the noncoordinating N center are shorter (av 1.58 Å) than the P−N(ring) bonds associated with metal coordination (av 1.63 Å). While the phosphazene rings of the free ligands **1**−**3** are planar or close to planarity,[9] the coordination to silver ions causes the rings to pucker, which is evident from the ring torsion angles exhibiting maximum values of 36.9° in (**1**)$_2$($AgClO_4$)$_3$, 29.3° in **1**($AgNO_3$)$_2$, 23.0° in **2**($AgClO_4$), 36.7° in **3**($AgClO_4$)$_2$, 36.7° in **3**($AgNO_3$)$_2$, 35.8° in **3**($AgClO_4$)($AgNO_3$), and 35.4° in **4**($AgClO_4$). Ring conformations include a *chair* in (**1**)$_2$($AgClO_4$)$_3$ and **1**($AgNO_3$)$_2$, a *half-chair* in **2**($AgClO_4$), a *boat* in (**1**)$_2$($AgClO_4$)$_3$, **3**($AgClO_4$)$_2$, and **3**($AgNO_3$)$_2$, and a *twisted boat* in **3**($AgClO_4$)($AgNO_3$) and **4**($AgClO_4$). As a result, the polymeric 1D and 2D arrangements comprising silver ions and phosphazene rings are corrugated. Two phosphazene rings linked by a linear N−Ag−N bridge are more or less coplanar or slightly tilted with respect to one another (Figure 9). This arrangement provides effective interlocking of the lipophilic side groups, which form bilayers around the inorganic frameworks of the coordination polymers. Figure 10 displays the corrugated supramolecular structure and the shielding effect of the lipophilic periphery by example of the polymeric complex **4**($AgClO_4$). Similarly, the hydrogen-bonded core structures of the parent phosphazenes are wrapped within the lipophilic periphery of exocyclic R groups.[9] Hydrogen-bonding distances in (**1**)$_2$($AgClO_4$)$_3$, **1**($AgNO_3$)$_2$, and **2**($AgClO_4$) are in the expected range for NH···O bonds involving inorganic oxo anions:[12] The N···O distances in NH···O bonds range from 2.94 to 3.24 Å in structures containing perchlorate ions and from 2.87 to 3.11 Å in structures of nitrate derivates. It

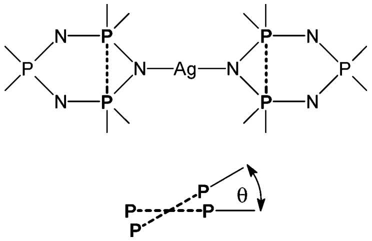

Figure 9. Tilting angle of two phosphazene rings linked by a linearly bridging silver ion, as defined by the dihedral angle θ between the two vectors joining P centers adjacent to the coordinating N atoms: (**1**)$_2$($AgClO_4$)$_3$, $\theta = 7.6°$, 13.7°, 20.8°; **1**($AgNO_3$)$_2$, $\theta = 4.2°$, 12.7°; **2**($AgClO_4$), $\theta = 0°$; **3**($AgClO_4$)$_2$, $\theta = 18.1°$; **3**($AgNO_3$)$_2$, $\theta = 15.5°$; **3**($AgClO_4$)($AgNO_3$), $\theta = 12.5°$; **4**($AgClO_4$), $\theta = 27.6°$.

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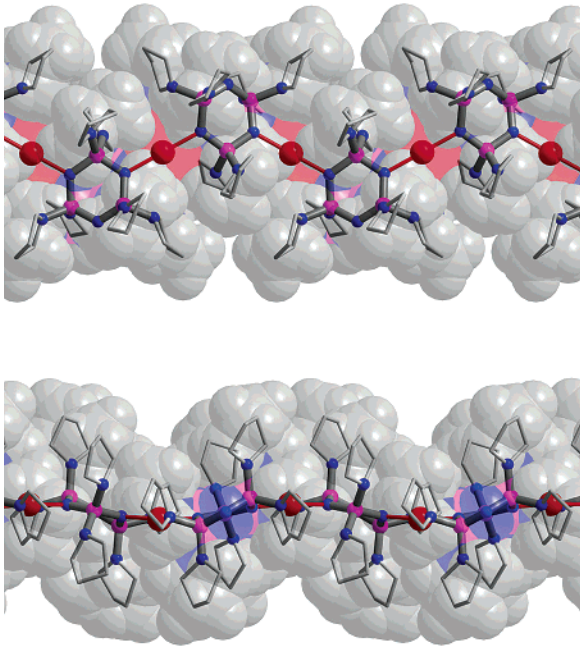

Figure 10. Two views of the superimposition of a space-filling diagram and a ball-and-stick model of **4**($AgClO_4$).

is also noteworthy that some of the crystal structures presented here exhibit chiral space groups. Complex **1**($AgNO_3$)$_2$ crystallizes in spacegroup *P*1, resulting in polar stacking of the supramolecular layers, and **4**($AgClO_4$) adopts space group $P2_12_12_1$, displaying a chiral chain structure.

Conclusion

We have shown that cyclophosphazenes, $(RNH)_6P_3N_3$, produce supramolecular coordination compounds in conjunction with silver salts by formation of linear N−Ag−N connections via N(ring) sites. Two phosphazene rings linked by a N−Ag−N bridge are aligned in a coplanar or almost coplanar fashion along the N−Ag−N axis. The ligands act as either trigonal planar or bidentate bent (120°) nodes, depending on the steric and electronic properties of the exocyclic groups R. In this way, control over the network topology of the coordination polymer is gained, leading to either 2D networks or 1D zigzag chain arrangements. (**1**)$_2$($AgClO_4$)$_3$ is the first example of a coordination polymer constructed from a 1,3,5-triazine-equivalent node that furnishes the formation of a (6,3) network. Lattice interpenetration, which is often encountered in conjunction with small networking ligands,[13] does not occur due to the steric factor of exocyclic R groups.[14] Straightforward side chain substitution at phosphorus allows fine-tuning of the steric effect of the lipophilic ligand periphery. The conformational freedom of the exocyclic amino groups has no direct effect on the network topology of the coordination polymer involving metal ions and phosphazene ligands, but smoothes the crystallization process by allowing effective interlocking of R groups and accommodation of anions within an adaptable H-bonding network. The ability to bind anions and metal cations simultaneously and the prospect of introducing further donor sites into side groups, R, promises interesting applications for cyclotriphosphazenes as polyfunctional and hemilabile ligands in supramolecular coordination compounds. It is noteworthy that cyclophosphazenes carrying organo amino substituents are of high chemical and thermal stability and, therefore, applicable in standard synthetic procedures leading to coordination networks and composite materials. This includes unlimited exposure to air, treatment with strong Brønsted acids and bases, and hydrothermal conditions.

Experimental Section

Synthesis. Phosphazenes **1**, **2**, **3**,[9] and **4**[10] were prepared as previously described. Crystalline materials (**1**)$_2$($AgClO_4$)$_3$, **1**($AgNO_3$)$_2$, **2**($AgClO_4$), **3**($AgClO_4$)$_2$, **3**($AgNO_3$)$_2$ and **4**($AgClO_4$) were obtained by careful layering a solution containing 300 mg of phosphazene ligand in 10 mL of methanol with a solution containing three molar equivalents of the silver salt in 10 mL of methanol. Crystals of **3**($AgClO_4$)($AgNO_3$) were obtained by layering a solution containing 300 mg of phosphazene ligand in 10 mL of methanol with a solution containing molar equivalents of $AgClO_4$ and $AgNO_3$ in 10 mL of methanol. *Caution should be used when handling perchlorate salts, since these can be explosive when dry!*

Data for (1)$_2$(AgClO$_4$)$_3$. Anal. Calcd for $C_{36}H_{96}Ag_3Cl_3N_{18}O_{12}P_6$: C, 27.21; H, 6.09; N, 15.87. Found: C, 27.41; H, 6.22; N, 15.68. IR (Nujol): $\nu(\mathrm{cm}^{-1}) = 3320$ (N−H), 1238, 1152 (P−N$_{\mathrm{ring}}$), 1089 (P−N$_{\mathrm{ring}}$), 921, 799, 740, 618. Yield: 430 mg (87%).

Data for 1(AgNO$_3$)$_2$. Anal. Calcd for $C_{18}H_{48}Ag_2N_{11}O_6P_3$: C, 26.26; H, 5.88; N, 18.71. Found: C, 26.50; H, 6.01; N, 18.60. IR (Nujol): $\nu(\mathrm{cm}^{-1}) = 3289$ (N−H), 1374, 1152 (P−N$_{\mathrm{ring}}$), 1104 (P−N$_{\mathrm{ring}}$), 1021, 930, 799. Yield: 430 mg (85%).

Data for 2(AgClO$_4$). Anal. Calcd for $C_{36}H_{72}AgClN_9O_4P_3$: C, 46.43; H, 7.79; N, 13.54. Found: C, 46.65; H, 7.91; N, 13.36. IR (Nujol): $\nu(\mathrm{cm}^{-1}) = 3298$ (N−H), 3143 (N−H), 1626, 1224, 1096 (P−N$_{\mathrm{ring}}$), 936, 772, 621. Yield: 310 mg (81%).

Data for 3(AgClO$_4$)$_2$. Anal. Calcd for $C_{42}H_{48}Ag_2Cl_2N_9O_8P_3$: C, 42.52; H, 4.08; N, 10.63. Found: C, 41.77; H, 3.91; N, 10.18. IR (Nujol): $\nu(\mathrm{cm}^{-1}) = 3351$ (N−H), 3318 (N−H), 1145 (P−N$_{\mathrm{ring}}$), 1095 (P−N$_{\mathrm{ring}}$), 1065 (P−N$_{\mathrm{ring}}$), 922, 787, 731, 694. Yield: 410 mg (89%).

Data for 3(AgNO$_3$)$_2$. Anal. Calcd for $C_{42}H_{48}Ag_2N_{11}O_6P_3$: C, 45.38; H, 4.35; N, 13.86. Found: C, 45.98; H, 4.79; N, 13.13. IR (Nujol): $\nu(\mathrm{cm}^{-1}) = 3375$ (N−H), 3263 (N−H), 1143 (P−N$_{\mathrm{ring}}$), 1091 (P−N$_{\mathrm{ring}}$), 1065 (P−N$_{\mathrm{ring}}$), 973, 908, 790, 734, 695. Yield: 390 mg (91%).

Data for 3(AgClO$_4$)(AgNO$_3$). Anal. Calcd for $C_{42}H_{48}Ag_2ClN_{10}O_7P_3$: C, 43.90; H, 4.21; N, 12.19. Found: C, 44.98; H, 4.77; N, 11.73. IR (Nujol): $\nu(\mathrm{cm}^{-1}) = 3339$ (N−H), 3293 (N−H), 1315, 1143 (P−N$_{\mathrm{ring}}$), 1089 (P−N$_{\mathrm{ring}}$), 1066 (P−N$_{\mathrm{ring}}$), 903, 799, 731, 690. Yield: 370 mg (82%).

Data for 4(AgClO$_4$). Anal. Calcd for $C_{24}H_{48}AgClN_9O_4P_3$: C, 37.78; H, 6.34; N, 16.52. Found: C, 38.06; H, 6.44; N, 16.27. IR (Nujol): $\nu(\mathrm{cm}^{-1}) = 1197$, 1084 (P−N$_{\mathrm{ring}}$), 916, 835, 735, 618. Yield: 280 mg (71%).

X-ray Crystallography. Selected bond lengths and angles are listed in Table 1, and crystallographic data are listed in Table 2. Crystallographic data were recorded on a Bruker Apex diffractometer equipped with a CCD detector using Mo Kα radiation ($\lambda = 0.71073$ Å) at $T = 150$ K. Semiempirical absorption corrections were applied (SADABS). Structures were solved by direct methods and refined by full-matrix least squares against F^2 using all data

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(13) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460.

(14) Xu, X.; Nieuwenhuyzen, M.; James, S. L. *Angew. Chem., Int. Ed.* **2002**, *41*, 764.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of Crystal Structures

(**1**)$_2$(AgClO$_4$)$_3$		**1**(AgNO$_3$)$_2$		**2**(AgClO$_4$)		**3**(AgClO$_4$)$_2$		**3**(AgNO$_3$)$_2$		**3**(AgClO$_4$)(AgNO$_3$)		**4**(AgClO$_4$)	
Ag1−N11	2.157(3)	Ag1−N11	2.217(9)	Ag1−N1	2.143(6)	Ag1−N1	2.354(3)	Ag1−N1	2.135(3)	Ag1−N1	2.260(2)	Ag1−N1	2.122(2)
Ag1′−N22	2.150(3)	Ag1−O11	2.399(10)	Ag2−N2	2.141(6)	Ag1−O1	2.398(3)	Ag1−N2′	2.118(3)	Ag1−O22	2.344(2)	Ag1−N3′	2.130(3)
Ag2−N13	2.128(3)	Ag1−O12	2.594(12)	P1−N1	1.607(6)	Ag1−C13	2.572(4)	Ag2−N3	2.239(4)	Ag1−C13	2.476(3)	P1−N1	1.628(2)
Ag2−N21	2.128(3)	Ag2−N12	2.104(9)	P1−N2	1.628(6)	Ag1−C23	2.531(4)	Ag2−O1	2.351(4)	Ag2−N2	2.134(2)	P1−N3	1.623(3)
Ag3−N23	2.164(3)	Ag2−N22′	2.116(9)	P2−N1	1.663(7)	Ag1−C22	2.663(4)	Ag2−C33	2.524(4)	Ag2−N3′	2.126(2)	P2−N1	1.631(2)
Ag3′−N12	2.156(3)	Ag3−N13	2.132(9)	P2−N3	1.575(6)	Ag2−N2	2.137(3)	P1−N1	1.613(3)	P1−N1	1.618(2)	P2−N2	1.583(3)
P11−N11	1.628(3)	Ag3−N23′	2.127(9)	P3−N2	1.636(6)	Ag2′−N3	2.133(3)	P1−N3	1.618(3)	P1−N3	1.619(2)	P3−N2	1.586(3)
P11−N13	1.625(3)	Ag4−N21	2.254(11)	P3−N3	1.579(7)	P1−N1	1.611(3)	P2−N1	1.616(3)	N1−P2	1.616(2)	P3−N3	1.626(3)
P12−N11	1.614(3)	Ag4−O21	2.453(12)	P1−N10	1.619(7)	P1−N3	1.622(3)	P2−N2	1.619(3)	P2−N2	1.626(2)	P1−N10	1.635(2)
P12−N12	1.617(3)	Ag4−O22	2.535(10)	P1−N40	1.638(6)	P2−N1	1.612(3)	P3−N2	1.614(4)	N2−P3	1.616(2)	P1−N40	1.636(3)
P13−N12	1.623(3)	Ag4−O31	2.494(9)	P2−N20	1.610(7)	P2−N2	1.624(3)	P3−N3	1.617(3)	P3−N3	1.625(2)	P2−N20	1.626(3)
P13−N13	1.617(3)	P11−N11	1.620(9)	P2−N50	1.654(7)	P3−N2	1.613(3)	P1−N10	1.625(4)	P1−N10	1.622(2)	P2−N50	1.645(3)
P11−N110	1.620(3)	P11−N13	1.622(11)	P3−N30	1.634(6)	P3−N3	1.621(3)	P1−N40	1.634(3)	P1−N40	1.644(3)	P3−N30	1.645(3)
P11−N140	1.640(4)	P12−N11	1.614(10)	P3−N60	1.619(7)	P1−N10	1.632(4)	P2−N20	1.615(4)	P2−N20	1.631(2)	P3−N60	1.620(3)
P12−N120	1.615(3)	P12−N12	1.633(9)	N1−Ag1−N1′	180.0	P1−N40	1.610(4)	P2−N50	1.623(4)	P2−N50	1.630(2)	N1−Ag1−N3′	175.64(9)
P12−N150	1.612(3)	P13−N12	1.631(9)	N2−Ag2−N2′	180.0	P2−N20	1.625(3)	P3−N30	1.625(4)	P3−N30	1.616(2)	N3−P1−N1	111.5(2)
P13−N130	1.616(4)	P13−N13	1.605(10)	N1−P1−N2	112.4(3)	P2−N50	1.625(3)	P3−N60	1.606(4)	P3−N60	1.634(2)	P1−N1−P2	122.3(2)
P13−N160	1.614(4)	P11−N110	1.679(11)	N1−P2−N3	112.2(3)	P3−N30	1.620(3)	N1−Ag1−N2′	176.22(14)	N2−Ag2−N3′	177.29(8)	N2−P2−N1	112.8(2)
P21−N21	1.626(3)	P11−N140	1.569(12)	N2−P3−N3	112.5(3)	P3−N60	1.626(3)	N1−P1−N3	110.69(17)	N1−P1−N3	109.87(1 1)	P2−N2−P3	123.9(2)
P21−N23	1.618(3)	P12−N120	1.646(12)	P1−N1−P2	124.3(4)	N2−Ag2−N3′	173.72(12)	P1−N1−P2	125.3(2)	P2−N1−P1	125.10(1 4)	N2−P3−N3	113.2(2)
P22−N21	1.636(3)	P12−N150	1.625(10)	P1−N2−P3	126.4(4)	N1−P1−N3	109.93(16)	N1−P2−N2	111.35(18)	N1−P2−N2	110.94(11)	P1−N3−P3	122.9(2)
P22−N22	1.615(3)	P13−N130	1.645(11)	P2−N3−P3	128.6(4)	P1−N1−P2	125.4(2)	P3−N2−P2	124.8(2)	P3−N2−P2	123.38(1 3)		
P23−N22	1.624(3)	P13−N160	1.617(11)			N1−P2−N2	110.46(16)	N2−P3−N3	110.77(17)	N2−P3−N3	111.82(1 1)		
P23−N23	1.609(3)	P21−N21	1.610(9)			P3−N2−P2	124.81(19)	P3−N3−P1	123.9(2)	P1−N3−P3	124.81(1 3)		
P21−N210	1.621(3)	P21−N23	1.624(11)			N2−P3−N3	112.09(16)						
P21−N240	1.618(3)	P22−N21	1.602(11)			P3−N3−P1	124.90(19)						
P22−N220	1.627(3)	P22−N22	1.608(11)										
P22−N250	1.618(3)	P23−N22	1.629(9)										
P23−N230	1.627(3)	P23−N23	1.631(12)										
P23−N260	1.629(3)	P21−N210	1.675(14)										
N11−Ag1−N22	174.64(12)	P21−N240	1.586(13)										
N13−Ag2−N21	177.10(13)	P22−N220	1.623(14)										
N12−Ag3−N23	177.17(12)	P22−N250	1.595(10)										
N11−P11−N13	111.0(2)	P23−N230	1.642(11)										
P11−N11−P12	124.0(2)	P23−N260	1.613(12)										
N11−P12−N12	111.7(2)	N12−Ag2−N22′	179.6(4)										
P12−N12−P13	123.0(2)	N13−Ag3−N23′	178.9(5)										
N12−P13−N13	110.9(2)	N11−P11−N13	110.5(5)										
P11−N13−P13	128.3(2)	P12−N11−P11	127.5(6)										
N21−P21−N23	109.8(2)	N11−P12−N12	110.1(5)										
P22−N21−P21	127.7(2)	P13−N12−P12	127.0(6)										
N21−P22−N22	109.6(2)	N13−P13−N12	110.5(5)										
P22−N22−P23	122.6(2)	P13−N13−P11	128.5(6)										
N22−P23−N23	112.7(2)	N21−P21−N23	110.7(6)										
P21−N23−P23	122.9(2)	P22−N21−P21	127.4(7)										
		N21−P22−N22	109.6(5)										
		P22−N22−P23	127.2(6)										
		N22−P23−N23	109.6(5)										
		P21−N23−P23	127.9(6)										

Table 2. Crystallographic Data

	(**1**)$_2$(AgClO$_4$)$_3$	**1**(AgNO$_3$)$_2$	**2**(AgClO$_4$)	**3**(AgClO$_4$)$_2$	**3**(AgNO$_3$)$_2$	**3**(AgClO$_4$)(AgNO$_3$)	**4**(AgClO$_4$)
empirical formula	$C_{36}H_{96}Ag_3Cl_3N_{18}O_{12}P_6$	$C_{18}H_{48}Ag_2N_{11}O_6P_3$	$C_{36}H_{72}AgClN_9O_4P_3$	$C_{42}H_{48}Ag_2Cl_2N_9O_8$	$C_{42}H_{48}Ag_2N_{11}O_6P_3$	$P_3C_{42}H_{48}Ag_2ClN_{10}O_7P_3$	$C_{24}H_{48}AgClN_9O_4P_3$
fw	1589.08	823.32	931.26	1186.44	1111.56	1149.00	762.94
cryst syst	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$P1$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_12_12_1$
a/Å	12.6987(5)	10.7287(12)	12.610(3)	15.0948(19)	15.021(2)	15.1730(8)	12.694(3)
b/Å	23.5481(10)	12.5147(14)	19.257(5)	12.3782(15)	12.4692(19)	12.4578(7)	13.083(2)
c/Å	21.5863(10)	12.5578(14)	19.014(5)	24.188(3)	23.851(4)	24.0214(13)	19.418(4)
α/deg	90	85.627(2)	90	90	90	90	90
β/deg	94.3530(10)	81.420(2)	108.153(5)	91.925(2)	90.659(3)	92.9330(10)	90
γ/deg	90	83.619(2)	90	90	90	90	90
V/Å^3	6436.3(5)	1653.8(3)	4387.5(19)	4516.9(10)	4467.0(12)	4534.6(4)	3224.9(11)
Z	2	2	4	4	4	4	4
μ(Mo Kα)/cm^{-1}	1.242	1.378	0.678	1.156	1.045	1.091	1.571
ρ(calcd)/g cm^{-1}	1.640	1.653	1.410	1.745	1.653	1.683	0.903
no. of reflns, total	33614	9943	22364	23330	22672	27844	19916
no. of reflns, unique	11336	8336	7728	7971	7867	10374	7354
R_{int}	0.043	0.020	0.102	0.052	0.108	0.019	0.034
$2\theta_{max}$/deg	50	56	50	50	50	56	56
T_{min}/T_{max}	0.783	0.849	0.734	0.834	0.641	0.915	0.933
no. of params	713	552	490	589	614	610	408
R1 ($F > 4\sigma(F)$)	0.038	0.059	0.072	0.039	0.046	0.035	0.032
wR2 (all data)	0.093	0.170	0.180	0.099	0.114	0.099	0.060
Flack param		0.03(5)					0.18(2)

(SHELXTL). All non-H atoms were refined anisotropically with the exception of disordered atoms. H atoms were fixed in calculated positions at parent C and N atoms, respectively. Disordered atoms were split on two positions and refined using similar distance and similar U restraints. This included one propyl group in (**1**)$_2$(AgClO$_4$)$_3$, two propyl groups and the non-metal-coordinated nitrate ion in **1**(AgNO$_3$)$_2$, the non-metal-coordinated nitrate ion in **3**(AgNO$_3$)$_2$, and three O atoms of the perchlorate ion in **4**(AgClO$_4$).

Acknowledgment. We thank the EPSRC for financial support.

Supporting Information Available: X-ray crystallographic data in CIF format for (**1**)$_2$(AgClO$_4$)$_3$, **1**(AgNO$_3$)$_2$, **2**(AgClO$_4$), **3**(AgClO$_4$)$_2$, **3**(AgNO$_3$)$_2$, **3**(AgClO$_4$)(AgNO$_3$), and **4**(AgClO$_4$). This material is available free of charge via the Internet at http://pubs.acs.org.

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