Introduction

Various intriguing molecular frames have been designed and assembled by the selection of basic components such as the coordination geometry of metal ions, the binding site of donating atoms, and the length of spacers or/and by the induction of weak intra- or intermolecular interactions. 1−10 Rational control of molecular frameworks via (counter)anions is rare due to the less effective electrostatic binding interactions. 11 Recently, however, anion coordination chemistry has become a rapidly emerging field owing to a timely interest from environmental pollution, industrial chemical, biological process, ionic liquids, catalysis, lithium battery, and health-related perspectives. 12−18 More recent developments include exciting advances in anion template assembly, ion-pair related perspectives. 12

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Subtle Role of Polyatomic Anions in Molecular Construction: Structures and Properties of AgX Bearing 2,4′-Thiobis(pyridine) (X− = NO3−, BF4−, ClO4−, PF6−, CF3CO2−, and CF3SO3−)

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Studies on the subtle effects and roles of polyatomic anions in the self-assembly of a series of AgX complexes with 2,4′-Py2S (X− = NO3−, BF4−, ClO4−, PF6−, CF3CO2−, and CF3SO3−; 2,4′-Py2S = 2,4′-thiobis(pyridine)) have been carried out. The formation of products appears to be primarily associated with a suitable combination of the skewed conformers of 2,4′-Py2S and a variety of coordination geometries of Ag(I) ions. The molecular construction via self-assembly is delicately dependent upon the nature of the anions. Coordinating anions afford the 1:1 adducts [Ag(2,4′-Py2S)X] (X− = NO3− and CF3CO2−), whereas noncoordinating anions form the 3:4 adducts [Ag3(2,4′-Py2S)3X3 (X− = ClO4− and PF6−)]. Each structure seems to be constructed by competition between π−π interactions of 2,4′-Py2S spacers vs Ag⋯X interactions. For ClO4− and PF6−, an anion-free network consisting of linear Ag(I) and trigonal Ag(I) in a 1:2 ratio has been obtained whereas, for the coordinating anions NO3− and CF3CO2−, an anion-bridged helix sheet and an anion-bridged cyclic dimer chain, respectively, have been assembled. For a moderately coordinating anion, CF3SO3−, the 3:4 adduct [Ag3(2,4′-Py2S)3]X3 (X− = ClO4− and PF6−) has been obtained similarly to the noncoordinating anions, but its structure is a double strand via both face-to-face (π−π) stackings and Ag⋯Ag interactions, in contrast to the noncoordinating anions. The anion exchanges of [Ag3(2,4′-Py2S)3]X3 (X− = BF4−, ClO4−, and PF6−) with BF4−, ClO4−, and PF6− in aqueous media indicate that a [BF4−]− analogous is isostructural with [Ag3(2,4′-Py2S)3]X3 (X− = ClO4− and PF6−). Furthermore, the anion exchangeability for the noncoordinating anion compounds and the X-ray data for the coordinating anion compounds establish the coordinating order to be NO3− > CF3CO2− > CF3SO3− > PF6− > ClO4− > BF4−.
recognition, and the function of anions in supramolecular chemistry.\textsuperscript{19–22} The features of anions such as negative charge, size, a wide range of geometries, significant solvent effects, and pH dependence imply that some anions play crucial roles in the self-assembly of functional molecules.\textsuperscript{23–25}

Our previous results on the reactions of $n,n'$-Py$_2$Y ($n = n' = 3$ or 4; $Y = O$, $S$, Me$_3$Si) with the Ag(I) ions showed a cylindrical molecular spring via the exchange of labile anions\textsuperscript{26–28} and a variety of coordination geometries of Ag(I) ions.\textsuperscript{26–30} Such symmetric bipyril spacer groups have been used as molecular tectonic elements, but the exploitation of 2,4'-thiobis(pyridine) (2,4'-Py$_2$S) has until recently remained unexplored. The 2,4'-Py$_2$S is a noninnocent ligand possessing interesting N–S–N angles, potential tridentate sites, and conformational nonrigidity.\textsuperscript{31,32} These structural properties may be useful in construction of elaborate metal compounds. Our primary purpose is to elucidate the direct roles of anions in the self-assembly of Ag(I) ion with the unique 2,4'-Py$_2$S bidirectional spacer. We describe here subtle effects and roles of polyatomic anions on the self-assembly of a series of AgX with 2,4'-Py$_2$S ($X^- = NO_3^-$, BF$_4^-$, ClO$_4^-$, PF$_6^-$, CF$_3$CO$_2$-, and CF$_3$SO$_3^-$). The stable polyatomic anions have been extensively employed for the isolation of cationic transition metal skeletons.

![2,4'-Py$_2$S](image)

**Experimental Section**

**Materials and Physical Measurements.** AgX and NaX ($X^- = NO_3^-$, BF$_4^-$, ClO$_4^-$, PF$_6^-$, CF$_3$CO$_2$-, and CF$_3$SO$_3^-$) were purchased from Strem and Junsei Chemical Co., respectively, and were used

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refined by full-matrix least-squares techniques (SHELXL 97). The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions and refined only for the isotropic thermal factors. For $[\text{Ag}(2,4′\text{-PyS})_2]\text{ClO}_4$, $\text{PF}_6^-$, a $\text{ClO}_4^-$ and a $\text{PF}_6^-$ anion, respectively, were disordered. For $[\text{Ag}(2,4′\text{-PyS})\text{NO}_3]$, the $\text{NO}_3^-$ anion lies in a special position. Crystal parameters and procedural information corresponding to data collection and structure refinement are given in Table 1.

### Results

#### Construction

The slow diffusion of an organic solution of 2,4′-PyS into an aqueous solution of 2AgX ($X^- = \text{NO}_3^-$, $\text{ClO}_4^-$, $\text{PF}_6^-$, $\text{CF}_3\text{CO}_2^-$, and $\text{CF}_3\text{SO}_3^-$) afforded two kinds of products, 1:1 adducts (for $\text{NO}_3^-$ and $\text{CF}_3\text{CO}_2^-$) and 3:4 adducts ($\text{Ag}(2,4′\text{-PyS})_2$) (for $\text{ClO}_4^-$, $\text{PF}_6^-$, and $\text{CF}_3\text{SO}_3^-$), presumably due to the coordinating nature of anions. Furthermore, each self-assembled structure is strongly dependent upon the anions (Scheme 1). The reaction of 2AgX ($X^- = \text{ClO}_4^-$ and $\text{PF}_6^-$) with 2,4′-PyS produces unique networks whereas treatment of 2AgX ($X^- = \text{NO}_3^-$ and $\text{CF}_3\text{CO}_2^-$) with 2,4′-PyS give anion-bridged infinite structures. The reaction of 2AgCF$_3$SO$_3$ with the same ligand affords adducts ($\text{Ag}(2,4′\text{-PyS})_2(\text{CF}_3\text{CO}_2)$).

### Crystal Structures

The molecular structure of $[\text{Ag}(2,4′\text{-PyS})_2]\text{ClO}_4^-$ is depicted in Figure 1, and selected data are listed in Table 2. Their skeletal structures are the same networks consisting of $\text{Ag}(\text{II})$ and 2,4′-PyS (3:4). Each 2,4′-PyS spacer connects two Ag(I) ions (Ag−N = 2.162(5)−2.295(6) Å) for $\text{ClO}_4^-$; 2.170(3)−2.268−(4) Å for $\text{PF}_6^-$ defining the edges of 64-membered rings. The network structure seems to be sustained by the presence of face-to-face (π−π) stackings of pyridine rings (3.6−3.8 Å). Linear Ag(I) and trigonal Ag(I) ions exist in a 1:2 ratio in the network structure. The linear Ag(I) ion is coordinated by two 4′-Py moieties ($\text{N}−\text{Ag}−\text{N} = 180.0(4)$° for $\text{ClO}_4^-$ and 180.0(3)$^\circ$ for $\text{PF}_6^-$). The trigonal Ag(I) ion is coordinated by a 4′-Py and two 2-Py ($\text{N}−\text{Ag}−\text{N} = 108.7(2)−130.3(2)$° for $\text{ClO}_4^-$; 114.6(1)−126.1(1)$^\circ$ for $\text{PF}_6^-$). The anions do not interact with the Ag(I) ion and exist as simple counteranions (the shortest $\text{Ag}(\text{I})−\text{X} > 3.1$ Å). The bond angles of C−S−C are 103.1(3)−105.1(3)$^\circ$ for $\text{ClO}_4^-$ and 103.0(2)−103.1(2)$^\circ$ for $\text{PF}_6^-$, which are similar to those of 3,3′-PyS analogues.

The structure of $[\text{Ag}(2,4′\text{-PyS})\text{NO}_3]$ is shown in Figure 2, and selected data are listed in Table 2. Each 2,4′-PyS links two Ag(I) ions to give a single helix consisting of alternating Ag(I) and 2,4′-PyS. The nitrate anions bridge each helix in a bidentate mode (Ag−O = 2.574(5) Å). The Ag−O length is shorter than the coordinated bond (2.65(1) Å) of the tetrahedral $[\text{Ag}(3,3′\text{-PyS})\text{NO}_3]$ species. Thus,
the local geometry of the Ag(I) ion approximates to a trigonal arrangement \((N\text{-}Ag\text{-}O = 116.2(3)^\circ; N\text{-}Ag\text{-}N = 153.8(3)^\circ; N\text{-}Ag\text{-}O = 86.1(3)^\circ)\). The N\text{-}Ag\text{-}N angle is splayed out compared to the normal trigonal arrangement but is significantly bent from a linear arrangement owing to the presence of the coordinating anion. For the helix, there are two units in each turn (the pitch, \(a\) axis = 13.498(2) Å). The helical pitch is much longer than that (7.430(2) Å) of \([\text{Ag}(3,3'\text{-Py}_2\text{O})](\text{NO}_3)\)\(^{26}\). The oblong cylindrical helices are arrayed in an alternate right-handed and left-handed fashion. The C\text{-}S\text{-}C angle within the 2,4\text{,}3'-Py_2S moiety is 103.4(4)°.

The structure of \([\text{Ag}(2,4\text{,}3'-\text{Py}_2\text{S})(\text{CF}_3\text{CO}_2)]\) is depicted in Figure 3, and selected data are listed in Table 2. The skeletal structure is a centrosymmetric cyclic dimer chain. The 16-membered cyclic dimer may be stabilized via a face-to-face \((\pi\text{-}\pi)\) stacking of two pyridine rings (3.5 Å). The \(\text{CF}_3\text{CO}_2^-\) anion weakly links the two cyclic dimers in a tridentate fashion (Ag\text{-}O(1)' = 2.59 Å; Ag\text{-}O(1) = 2.67 Å; Ag\text{-}O(2) = 2.63 Å). The bridged tridentate bonding mode of \(\text{CF}_3\text{CO}_2^-\) anion is very rare. Thus, the local geometry of each Ag(I) ion is pseudo square pyramidal. The C\text{-}S\text{-}C angle (106.2(2)°) is relatively splayed out to sustain the cyclic dimer.

The molecular structure of \([\text{Ag}_3(2,4\text{,}3'-\text{Py}_2\text{S})_4](\text{CF}_3\text{SO}_3)_3\) is depicted in Figure 4, and selected data are listed in Table 2. The skeletal structure is a unique double-strand consisting of Ag(I) and 2,4\text{,}3'-Py_2S (3:4). Each 2,4\text{,}3'-Py_2S spacer connects two Ag(I) ions (Ag\text{-}N = 2.133(7)−2.425(9) Å). The two strands interact significantly via both face-to-face \((\pi\text{-}\pi)\)
The anion exchangeability of the anions of the network exchanged completely with the octahedral PF$_6^-$ ions. The tetrahedral Ag(I) ion and tetrahedral Ag(I) ion exist in a ratio of 2:1 in the crystal structure. The T-shaped Ag(I) ion is coordinated by two 4'-Py moieties (N$=$Ag$=$N = 94.6(3)–135.8(2)$^\circ$). The anions are positioned around the Ag(I)⋯Ag(I) interactions (3.226(1) Å). The T-shaped Ag(I) ion is coordinated by four 2-Py moieties (N$=$Ag$=$N = 171.5(3)–172.6(3)$^\circ$) and a neighboring Ag(I) ion (N$=$Ag$=$Ag = 84.4(2)–103.7(2)$^\circ$). The slightly bent angles of N$=$Ag$=$N support the presence of the Ag(I)⋯Ag(I) interactions. The tetrahedral Ag(I) ion is coordinated by four 2-Py moieties (N$=$Ag$=$N = 94.6(3)–135.8(2)$^\circ$). The anions are positioned around the silver ions (Ag⋯O = 3.05 Å). The bond angles of C$=$S$=$C are in the range of 103.1(4)–106.3(4)$^\circ$.

**Anion Exchange and Thermal Stability.** Anion exchange was achieved for the same network structures. The anion exchange of [Ag$_3$(2,4'-Py$_2$S)$_4$(ClO$_4$)$_3$] with PF$_6^-$ occurs smoothly in a typical aqueous media.$^{34,35}$ For [Ag$_3$(2,4'-Py$_2$S)$_4$(ClO$_4$)$_3$], the ClO$_4^-$ anions of the network exchanged completely with the octahedral PF$_6^-$ anions. The anion exchange procedure could be monitored by the characteristic IR bands of the anions. The exchange in aqueous media at room temperature was checked after 0, 3, 6, and 24 h (Figure 5).

![Figure 3. Asymmetric unit (top) and infinite structure (bottom) of [Ag(2,4'-Py$_2$S)(CF$_3$CO$_2$)].](image3.png)

![Figure 4. Asymmetric unit (top) and infinite structure (bottom) of [Ag$_3$(2,4'-Py$_2$S)$_4$(CF$_3$SO$_3$)$_3$]. For the infinite structure, the CF$_3$SO$_3^-$ counteranions were omitted for clarity.](image4.png)

![Figure 5. IR (KBr pellet) spectra during the anion exchange of [Ag$_3$(2,4'-Py$_2$S)$_4$(ClO$_4$)$_3$] with NaPF$_6$ after 0 h (a), after 3 h (b), after 6 h (c), and after 24 h (d). $\bullet$ and $\odot$ denote ClO$_4^-$ and PF$_6^-$ bands, respectively.](image5.png)

5). The infrared spectra show the gradual disappearance of intense ClO$_4^-$ bands (1088 cm$^{-1}$) and the appearance and growth of new PF$_6^-$ bands (832 cm$^{-1}$). The ClO$_4^-$ peaks disappear completely after 24 h. The other peaks of the spectrum remain virtually unchanged, suggesting that the skeletal structure is preserved during the anion exchange process. The elemental analysis and IR spectrum of the exchanged species are the same with those of the sample obtained by the direct reaction of AgPF$_4$ with 2,4'-Py$_2$S, indicating that the same compound is formed by the two different procedures. The X-ray powder diffraction patterns (Supporting Information) indicate that the two compounds are chemically identical. For the two exchanged samples, the high-angle peaks ($2\theta > 40^\circ$) do not appear due to the intrinsic low crystallinity of the samples. The reverse exchange, that is, the exchange of [Ag$_3$(2,4'-Py$_2$S)$_4$(PF$_6$)$_3$] with ClO$_4^-$, occurs only slightly after 2 days. To elucidate the structure of the [BF$_4^-$] analogue indirectly, the anion exchange of the [BF$_4^-$] analogue with PF$_6^-$ was also accomplished. The elemental analysis, IR, and X-ray powder diffraction pattern of the exchanged samples are identical to those of [Ag$_3$(2,4'-Py$_2$S)$_4$(PF$_6$)$_3$] prepared by the direct method, suggesting that the skeletal structure of the [BF$_4^-$] analogue is isostructural with [Ag$_3$(2,4'-Py$_2$S)$_4$(PF$_6$)$_3$]. Exchange of [Ag$_3$(2,4'-Py$_2$S)$_4$(ClO$_4$)$_3$] with BF$_4^-$ does not occur. The exchange of [Ag$_3$(2,4'-Py$_2$S)$_4$(ClO$_4$)$_3$] with BF$_4^-$ does not occur, but its reverse exchange occurs. The anion exchanges among the three similar skeletal structures are summarized in Scheme 2. Thus, the anion exchangeability seems to be governed by the nature of the anions$^{36}$ as well as the ionic character. Although all experiments including the preparation and anion exchange are carried out either in aqueous solutions or in aqueous suspensions, none of the compounds contain solvate water molecules. This is presum-


ably due to the intrinsic properties of the hydrophobic 2,4'-Py2S moiety. Moreover, there are no cavities that are large enough to accommodate guest molecules such as methanol and water.

The thermal analyses have been used to establish a relationship between structure and properties.37,38 The thermal stabilities of the present compounds are dependent upon each structure (Supporting Information). The decomposition temperatures of the 1D structures, [Ag(2,4'-Py2S)(CF3CO2)2] (190 °C) and [Ag(2,4'-Py2S)4](CF3SO3)2 (195 °C), are lower than those of the 2D structures, [Ag3(2,4'-Py2S)6](ClO4)3 (230 °C) and [Ag3(2,4'-Py2S)6](PF6)3 (210 °C). The [Ag(2,4'-Py2S)4(NO3)] compound decomposes at 200 °C. For [Ag3-(2,4'-Py2S)6](ClO4)3, the perchlorate anions appear to explode and fragment at the decomposition temperature, and thus, the perchlorate anions do not exist safely above 230 °C.

Discussion

Our intentional combinations of stable conformers of 2,4'-Py2S and a variety of Ag(I) ions have formed a series of anion-dependent motifs. Each motif was efficiently constructed irrespective of the stoichiometry, the solvent type, and the concentration. First of all, why were products of two ratios (1:1 and 3:4) formed? The ClO4- and PF6- anions have been considered as common “noncoordinating” anions.39 They have relatively little tendency to serve as ligands in the present structures. Such noncoordinating anions afford the spacer-abundant species, that is 3:4 adducts. On the other hand, the coordinating anions NO3- and CF3CO2- afford the 1:1 adducts. In the case of the noncoordinating anions, the forces used to sustain the skeletal network are the usual slipped π–π interactions.40 In contrast, the NO3- anion was coordinated to Ag(I) ion as shown by N–Ag(I)–N (153.8(3)°) and the Ag–O (2.574(5) Å). The coordinating NO3- is an obstacle to the construction of such a 2D network with π–π interactions and instead induces a helical sheet via a suitable spacer conformation. The CF3CO2- anion was weakly bridged to the two Ag(I) ion in a tridentate manner to give the anion-bridged cyclic dimer chain. For the CF3SO3-, the coordinating ability lies somewhere between that of the coordinating anions and the noncoordinating anions. The anion affords the 3:4 adduct like the noncoordinating anions, and the shortest Ag(I)···CF3SO3- (3.05 Å) distance is less than the sum of the van der Waals radii (3.20 Å) of Ag and O.41 The weak interaction seems to obstruct the formation of the 2D networks. From the Ag(I):2,4'-Py2S ratios in the products and the Ag···X distances (Table 2), the coordinating nature of the anions may be ordered as NO3- > CF3CO2- > CF3SO3- > PF6- and ClO4-. This order of NO3- > ClO4- is consistent with the Hofmeister series that is usually given in terms of the ability of anions to stabilize the structure of macromolecules.16 Furthermore, the present work can propose “a modified Hofmeister series” available for other polyatomic anions besides NO3- and ClO4-.

The overall motifs including the local geometry and molar ratios of the products appear to be delicately associated with the nature of anions. The slipped π–π interactions and the Ag···X interactions are competitive in constructing the present molecular structures. This study examines on the change in Ag···X interactions relative to the constant π–π interactions of the 2,4'-Py2S. These features may be schematically summarized in terms of a relative competition (presented by an arbitrary slope) between Ag···X interactions and π–π interactions in the self-assembly of Ag(I) compounds as shown in Figure 6.

To the right of the crossing point (CF3SO3-), the Ag···X interactions gradually weaken and the π–π interactions are more significant.40 To the left of the crossing point, the Ag···X interactions play an important role in the molecular construction. Since it forms a compound isostructural to [Ag3(2,4'-Py2S)6](ClO4)3, the BF4- anion can be categorized in noncoordinating class such as PF6- and ClO4-. Since the anion exchangeability is related to anion binding,12 the coordinating order of PF6-, ClO4-, and BF4- anions was determined by anion exchange. That is, [Ag3(2,4'-Py2S)6](ClO4)3 was easily exchanged by PF6-. Furthermore, the anion exchange of the [Ag3(2,4'-Py2S)6](BF4)3 analogue with PF6- was accomplished, but the exchange of the [Ag3(2,4'-Py2S)6](PF6)3 analogue with ClO4- or BF4- was limited. The anion exchange properties show that the coordinating nature of the anions is in the order: PF6- > ClO4- > BF4-. The coordinating nature is consistent with the order of association constants.42 Thus, the coordinating nature of all anions can be summarized in the order NO3- > CF3CO2- > CF3SO3-.
> PF₆⁻ > ClO₄⁻ > BF₄⁻. The weak nucleophilicity and strong electron-withdrawing nature of fluorine atom as well as Lewis acidic character of the boron atom may be major factors contributing to the least coordinating ability of BF₄⁻.

Conclusions

The first metal complexes of 2,4'-Py₂S demonstrate that the spacer is a fascinating tectonic unit without any particular strain in the construction of variable skeletons. The nonrigid 2,4'-Py₂S spacer is responsive to the nature of anions. A new coordinating series of polyatomic anions has been quantitatively determined via the structural analyses and the anion exchanges. The anion series can be extended as a crucial factor for the design and development of metal-based desirable materials such as anion sensors, molecular control, ion exchangers, chemical delivery, and intercalators.

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Supporting Information Available: Crystallographic data for [Ag(2,4'-Py₂S)(NO₃)], [Ag₃(2,4'-Py₂S)₄](ClO₄), [Ag₃(2,4'-Py₂S)₄](PF₆), [Ag(2,4'-Py₂S)(CF₃CO₂)], and [Ag₃(2,4'-Py₂S)₄](CF₃SO₃), IR spectra and X-ray powder diffraction patterns of [Ag₃(2,4'-Py₂S)₄](PF₆), prepared by the anion exchange of [Ag₃(2,4'-Py₂S)₄](BF₄), with PF₆⁻, and TGA traces of [Ag(2,4'-Py₂S)(NO₃)], [Ag₃(2,4'-Py₂S)₄](ClO₄), [Ag₃(2,4'-Py₂S)₄](PF₆), [Ag₃(2,4'-Py₂S)(CF₃CO₂)], and [Ag₃(2,4'-Py₂S)₄](CF₃SO₃). This information is available free of charge via the Internet at http://pubs.acs.org.

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