Conversion of Molecular Helical Springs to Chicken-wire Grids

Ok-Sang Jung,* Yun Ju Kim, Young-A Lee, Kyung Ho Yoo, and Hee K. Chae†

Materials Chemistry Laboratory, Korea Institute of Science and Technology, Seoul 136-791, Korea
†Department of Chemistry, Hankuk University of Foreign Studies, Yongin 449-791, Korea
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Introduction

Open framework structures are of great interest due to their mimicry of microporous solids useful for molecular adsorption,[1] host-guest chemistry,[2] ion exchange,[3,4] and unusual molecular mechanics.[5,6] Recent environmental concern about harmful anions has spurred new field of the open frameworks for reversible encapsulation and removal of such anions.[7] Such frameworks by the assembly of metal coordination species can be designed according to the selection of basic components such as the coordination geometry of the metal ions, the binding site of the donating atoms, and the length of the spacer.[8-14] However, the discovery of intriguing molecular frames has still been serendipitous since the structures are frequently influenced by the reaction conditions. Thus, control of a unique morphology by external perturbation has been an important field for the synthesis of functional supramolecules.[15]

We previously reported that the infinite helices, $[Ag(Py_2O)]X$ (Py_2O=3,3-oxybispyridine; $X^-=NO_3^-$, BF_4^-, ClO_4^-, and PF_6^-), are constructed and operated by the volume of the anion guests.[16] For the helices, the nonrigid interannular dihedral angles between two pyridyl groups around O and Ag atoms act as hinges of the helical subunit. In this context, we describe studies on the conversion of the ideal cylindrical helix, $[Ag(Py_2O)]BF_4$, to the chicken-wire grid, $[Ag(Py_2O)_2]BF_4$. The anion exchangeability of the new network structure was attempted. Tetrafluoroborate, perchlorate, and hexafluorophosphate that frequently appear in chemistry, environmental pollution, disease pathway, and biological processes[17,18] were selected as the anionic balancer of the cationic wire skeleton.

Experimental Section

Materials and Physical Measurements. NaX ($X^-=BF_4^-$, ClO_4^-, and PF_6^-) were purchased from Junsei Chemical Co. and used as received. $[Ag(Py_2O)]BF_4$ was prepared by the literature procedure.[16] Elemental microanalyses (C, H, N) were performed on crystalline samples by the Advanced Analytical Center at KIST using a Perkin Elmer 2400 CHNS analyzer. X-ray powder diffraction data were recorded on a Rigaku RINT/DMAX-2500 diffractometer at 40 kV, 126 mA for Cu Ka. Thermal analyses were performed under N_2 at a scan rate of 5 °C/min using a Stanton Red Croft TG 100. Infrared spectra were obtained on a Perkin Elmer 16F PC FTIR spectrophotometer with samples prepared as KBr pellet.

Preparation of $[Ag(Py_2O)_2]BF_4$: $[Ag(Py_2O)]BF_4$ (270 mg, 0.5 mmol) was solved in water (100 mL) at 75 °C and stirred for 1 h at the temperature. The residue solid was filtered off. The solution was very slowly cooled and left at 30 °C. The colorless crystals of $[Ag(Py_2O)_2]BF_4$ were obtained in 76% yield in two days. Anal. Calcd for $C_{20}H_{16}N_4AgBF_4O_2$: C, 44.56; H, 2.99; N, 10.39. Found: C, 44.30; H, 2.88; N, 10.24. IR (KBr, cm^{-1}): ν (BF_4), 1060 (s, multibands).

Counteranion Exchange. The procedure of a typical counteranion exchange is outlined: an aqueous solution (5 mL) of $NaClO_4$ (37 mg, 0.32 mmol) was added to a suspension of microcrystalline $[Ag(Py_2O)_2]BF_4$ (54 mg, 0.10 mmol) in water (10 mL) at room temperature. The reaction mixture was stirred, and the precipitates after 1, 3, 6, 12, and 24 h were monitored by IR spectra. After 24 h, the reaction mixture was filtered, and washed with several aliquots of water and methanol. Anal. Calcd for $[Ag(Py_2O)_2]ClO_4$ ($C_{20}H_{16}N_4AgClO_6$): C, 43.54; H, 2.92; N, 10.16. Found: C, 43.30; H, 2.87; N, 10.09. The counteranion exchange of $[Ag(Py_2O)_2]BF_4$ with PF_6^- was similarly achieved. Anal. Calcd for $[Ag(Py_2O)_2]PF_6$ ($C_{20}H_{16}N_4AgF_6O_2P$): C, 40.22; H, 2.70; N, 9.38. Found: C, 40.30; H, 2.67; N, 9.19. The exchanged species still gives a sharp X-ray powder diffraction pattern. The exchanged species were characterized by IR spectrum, X-ray powder diffraction, and elemental analysis.

Crystallographic Structure Determination. A colorless crystal of $[Ag(Py_2O)_2]BF_4$ ($0.36 \times 0.28 \times 0.20$ mm) was selected for the structure determination. All X-ray data were collected on an Enraf-Nonius CAD4 automatic diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) at ambient temperature. Unit cell dimensions were based on 25 well-centered reflections by using a least-square procedure. The crystal forms in the monoclinic crystal system. During the data collection, three standard reflections monitored after every hour did not reveal any systematic variation in intensity. The structure was solved by the SHELXS 97, and refined by SHELXL 97.[19] The nonhydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions and refined only for the isotropic thermal factors. Crystal parameters and procedural information corresponding to data collection and structure refinement were given in Table 1.

*To whom correspondence should be addressed. e-mail: Tel: +82-2-958-5086; Fax: +82-2-958-5089; e-mail: oksjung@kist.re.kr

Table 1. Crystallographic Data for $[Ag(Py_2O)_2]BF_4$

formula	$C_{20}H_{16}N_4AgBF_4O_2$
f.w.	539.05
space group	$P2_1cn$
a, Å	7.477(2)
b, Å	16.201(2)
c, Å	16.556(2)
V, Å^3	2005.5(6)
Z	4
d_{cal}, gcm^{-3}	1.785
μ, mm^{-1}	1.068
R {I>2σ(I)}	R1 = 0.0291
	wR2 = 0.0726

R1 = $\Sigma||Fo|-|Fc||/\Sigma|Fo|$. wR2 = $\Sigma w(Fo^2-Fc^2)^2/\Sigma wFo^4)^{1/2}$

Results and Discussion

Preparation and Crystal Structure. The recrystallization of $[Ag(Py_2O)]BF_4$ after dissolving at 75 ºC was converted to $[Ag(Py_2O)_2]BF_4$ in contrast to the recrystallization at room temperature. Moreover, the direct reaction of Ag(I) with Py_2O at room temperature even in the mole ratio of 1 : 2 produced the helical molecule, $[Ag(Py_2O)]BF_4$,[16] instead of the present compound, $[Ag(Py_2O)_2]BF_4$. The formation of a different structure appears to be primarily associated with a change of dihedral angle in the Py_2O at the high temperatures, indicating that the reaction temperature is a significant factor in the construction of molecular motifs.

The asymmetric unit and the extended structure of $[Ag(Py_2O)_2]BF_4$ are shown in Figure 1, and selected bond lengths and angles are listed in Table 2. The local geometry of the silver(I) center is a tetrahedral arrangement with four nitrogen donors (Ag-N(1), 2.35(1) Å; Ag-N(2), 2.32(1) Å; Ag-N(3), 2.51(1) Å; Ag-N(4), 2.53(1) Å). Each Py_2O spacer is linked to the two Ag(I) atoms *via* a bridge fashion, resulting in an infinite 32-membered $[Ag(I)]_4$ chicken-wire grid. The two diagonal Ag···Ag distances within the $[Ag(I)]_4$ unit are 7.48 Å and 16.20 Å. The Ag···Ag distances*via* a Py_2O linker is 8.92 Å. The geometry around the silver metal is severely distorted to sustain the grid (N-Ag-N, 75.7(2)-153.5(3)º). The dihedral angles of two pyridyl groups around the O atom are 59.2(5)-60.0(5)º, which are prominently different from that (74.3(2)º) of the helical structure, $[Ag(Py_2O)]BF_4$.[16] Interestingly, a counteranion is nestled in each rhombus *via* the weak electrostatic interactions with the Ag(I) cationic skeleton (the shortest Ag···F, 2.93-3.08Å), suggesting that the molecular chicken-wire network is anion exchange materials.

Anion Exchange and Thermal Properties. Although the wire grid suggests an ideal anion exchanger, it does not by itself prove that the grid behaves as anion exchanger. To investigate the exchange procedure, the counteranion exchange of $[Ag(Py_2O)_2]BF_4$ with PF_6^- was monitored by the characteristic IR bands of counteranions.[20] The exchange in water at room temperature was checked after 6, 12, and 24 h (Figure 2). The infrared spectra show the gradual disappearance of intense BF_4^- peaks (1060 cm^{-1}) and the appearance and

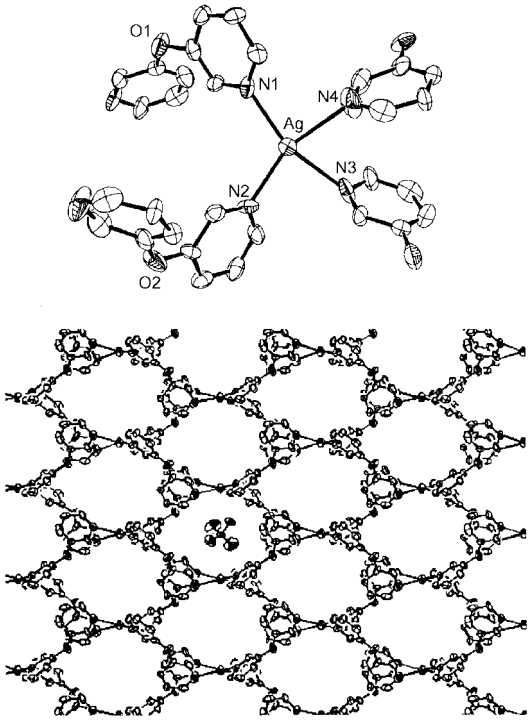


Figure 1. Asymmetric unit (up) and infinite network structure (down) of $[Ag(Py_2O)_2]BF_4$. Only a counteranion was presented for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (º) for $[Ag(Py_2O)_2]BF_4$

Ag-N(1)	2.35(1)	Ag-N(2)	2.32(1)
Ag-N(3)	2.51(1)	Ag-N(4)	2.53(1)
N(1)-Ag-N(2)	112.3(2)	N(2)-Ag-N(3)	88.4(3)
N(1)-Ag-N(3)	153.5(3)	N(2)-Ag-N(4)	152.1(4)
N(1)-Ag-N(4)	90.4(4)	N(3)-Ag-N(4)	75.7(2)
C(4)-O-C(14)'	123(1)	C(9)-O-C(19)'	121(1)

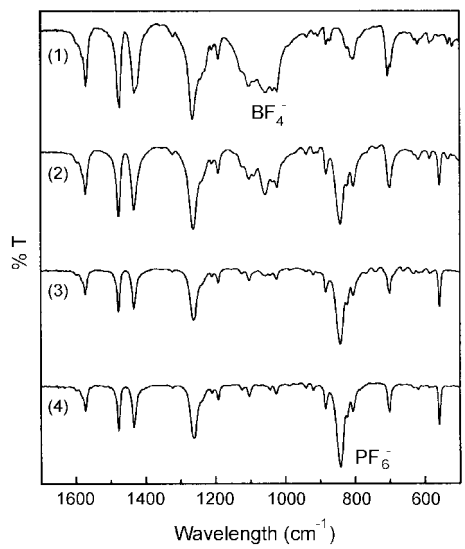
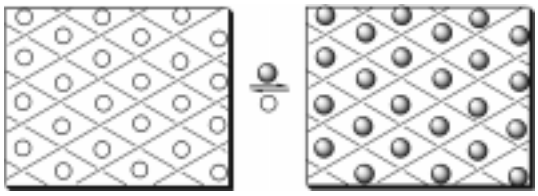


Figure 2. (a) IR (KBr pellet) change procedure during the counteranion exchange of $[Ag(Py_2O)_2]BF_4$ with $NaPF_6$. (1) $[Ag(Py_2O)_2]BF_4$ (2) after 6 h, (3) after 12 h, and (4) after 24 h.



Scheme 1

growth of new PF_6^- peaks around 842 cm^{-1}. The BF_4^- peaks disappear completely after 24 h. The other peaks of the spectra remain virtually unchanged. The counteranions are easy to be exchanged as shown in Scheme 1, but the exchange rate is some or less dependent upon the counteranions, the temperature, the mole ratio, and the concentration. The exchange with ClO_4^- was easily accomplished under the similar conditions, but $[Ag(Py_2O)_2]NO_3$ was not precipitated by the counteranion exchange presumably due to the water-solubility of $[Ag(Py_2O)_2]NO_3$. The solubility of $[Ag(Py_2O)_2]NO_3$ may stem from the small hydrophilic NO_3^- (36.0 cm^3/mol) for the rhombic frame ascribes. For instance, the anions of BF_4^- (51.0 cm^3/mol) is similar to ClO_4^- (52.1 cm^3/mol) and PF_6^- (56.2 cm^3/mol) in size.[16] All the exchanged species were characterized by the X-ray powder diffraction patterns, elemental analyses, and IR spectra. Though all experiments including the preparation and the counteranion exchange were carried out either in aqueous solutions or in water-containing solutions, the infinite cationic grid contains no solvate water molecules. This fact implies a significant structural behavior, *i.e.*, there are no extra-spaces that are large enough to accommodate other small guest molecules into the grid.

The traces of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) indicate that the compound has a reasonable degree of thermal stability in the solid state as shown in Figure 3. The TGA trace shows a weight loss corresponding to a Py_2O ligand (obs. 32.0%, calc. 31.9%) in the temperature range 158-181 ºC (eq 1), and further decomposition in the 300-330 ºC (eq 2). In particular, the thermal behavior in the range 300-330 ºC is very similar to the decomposition-temperature of helical $[Ag(Py_2O)]BF_4$.

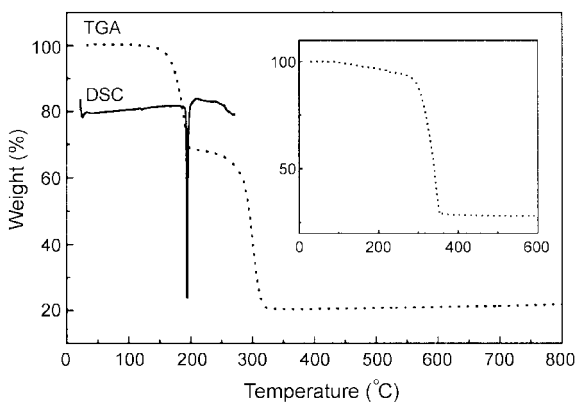


Figure 3. Overlay of TGA and DSC traces of $[Ag(Py_2O)_2]BF_4$, each recorded at heating rate of 5 ºC min^{-1}. The TGA curve in box was taken on the helical structure, $[Ag(Py_2O)]BF_4$.

This fact suggests that the structure of the thermal intermediate is similar to the helical structure.

$$[Ag(Py_2O)_2]BF_4 \xrightarrow{158\text{-}181\ ^\circ C} [Ag(Py_2O)]BF_4 + \text{fragmented } Py_2O \quad (1)$$

$$[Ag(Py_2O)]BF_4 \xrightarrow{300\text{-}330\ ^\circ C} \text{further decomposition} \quad (2)$$

Conclusions

The thermal driven recrystallization may be used to the development of a tailored synthetic strategy that is not possible by general methods. For the chicken-wire grid, their counteranions have been reversibly exchanged with the similar anions. The molecular grid may contribute to the development of molecular-based anion-exchangers.

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Supporting Information Available: Crystallographic data for $[Ag(Py_2O)_2]BF_4$. X-ray powder diffraction patterns of $[Ag(Py_2O)_2]X$ (X^-=BF_4, ClO_4^-, and PF_6^-). This information is available from OSJ.

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