

Helical Structure and Related Properties of Ag(I) Complex with 2,3-Bis(2-pyridyl)pyrazine

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Introduction

The induction of helical motif is now of great interest^{1,2} since the morphology have practical implication in multi-disciplinary areas such as templating precursors,³ memory devices,^{4,5} biomimetic chemistry,^{6,7} chiral chemistry,⁸ DNA,⁹ and structural biology.¹⁰ Such helical molecules 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.¹¹⁻¹³ We previously reported some ideal cylindrical springs that reversibly stretch via counteranion exchange.¹⁴⁻¹⁶ The key tectonic elements of the helical springs are the skewed conformer with nonrigid inter-annular dihedral angles and the coordination mode of silver(I). Thus, various ligands have been used for molecular helical building blocks,¹¹ but the exploitation of 2,3-bis(2-pyridyl)pyrazine (bpp) as a helical component has until recently remained unprecedented. The bpp is a noninnocent ligand possessing magic angles, potential tetradentate sites, and conformational nonrigidity.¹⁷⁻¹⁹ Moreover, the ligand would not be constrained to a planar conformation owing to the presence of intrinsic crowdedness between the two pyridyl groups. Such structural properties involving an inter-annular C-C bond between two aromatic rings could be widely used in construction of elaborate metal complexes.²⁰⁻²² In this context, we report the helical structure and related properties of (bpp)Ag(I) species.

Experimental Section

Materials and Physical Measurements. [Ag(CH₃CN)₄]BF₄ was purchased from Strem Co. and used without further purification. 2,3-Bis(2-pyridyl)pyrazine (bpp) was prepared according to the procedure of Goodwin and Lions.¹⁷ Elemental microanalyses (C, H, N) were performed on crystalline samples by the Advanced Analytical Center at KIST. Thermal analyses were performed under dinitrogen at a scan rate of 5 °C/min with a Stanton Red Croft TG 100. Infrared spectra were obtained on a Perkin Elmer 16F PC FTIR spectrophotometer with samples prepared as KBr pellets.

Preparation of [Ag(bpp)(CH₃CN)]BF₄·CH₃CN: An aceto-

nitrile solution (15 mL) of [Ag(CH₃CN)₄]BF₄ (180 mg, 0.5 mmol) and bpp (115 mg, 0.5 mmol) was stirred for 5 min at room temperature. The solution was slowly evaporated to obtain colorless crystals suitable for X-ray crystallography in 74% yield. IR (KBr, cm⁻¹): 3048 (w), 2252 (w, ν(CN)), 1585 (m), 1480 (m), 1392 (s), 1300 (w), 1107 (s), 1089 (s), 1058(s), 1034(s), 854(w), 790 (s), 748 (m), 570 (w). Elemental analysis (C, H, N) gave erratic results presumably due to the partial evaporation of solvate acetonitrile molecules.

Crystallographic Structure Determination. A colorless crystal of [Ag(bpp)(CH₃CN)]BF₄·CH₃CN (0.52 × 0.38 × 0.24 mm) was selected. The crystal was wedged in a Lindemann capillary with mother solvent. All X-ray data were collected on an Enraf-Nonius CAD4 automatic diffractometer with graphite-monochromated MoKα (λ = 0.71073 Å) at ambient temperature. Unit cell dimensions were based on 25 well-centered reflections by using a least-squares procedure. 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 97.²³ The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions and refined only for the isotropic thermal factors. The hydrogen atoms of acetonitrile molecules were not refined. Crystal parameters and procedural information corresponding to data collection and structure refinement were given in Table 1.

Table 1. Crystallographic Data for [Ag(bpp)(CH₃CN)]BF₄·CH₃CN

formula	C ₁₆ H ₁₃ N ₅ AgBF ₄ ·CH ₃ CN
f.w.	511.04
space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	19.379(4)
<i>b</i> , Å	7.731(1)
<i>c</i> , Å	13.973(2)
β, °	94.94(1)
<i>V</i> , Å ³	2085.5(6)
<i>Z</i>	4
<i>d</i> _{calc} , gcm ⁻³	1.70
μ, mm ⁻¹	1.017
R { <i>I</i> > 2σ(<i>I</i>)}	R ₁ = 0.0456
	wR ₂ = 0.1260

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad wR_2 = \sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4)^{1/2}$$

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Results

Construction and Crystal Structure. The slow diffusion of an acetonitrile solution of $[\text{Ag}(\text{CH}_3\text{CN})_4]\text{BF}_4$ and bpp afforded single crystals of the 1 : 1 adduct (Ag : bpp) in high yield. The formation of the adduct was not significantly affected by the mole ratio and concentration of the reactants. The product is insoluble in water and common organic solvents. The asymmetric unit and the extended structure of $[\text{Ag}(\text{bpp})(\text{CH}_3\text{CN})]\text{BF}_4 \cdot \text{CH}_3\text{CN}$ are shown in Figure 1, and selected bond lengths and angles are listed in Table 2. The local geometry of the silver(I) ion is a three-coordinate arrangement with three nitrogen donors (Ag-N(1), 2.368(3) Å; Ag-N(3), 2.331(3) Å; Ag-N(4), 2.283(4) Å). The silver

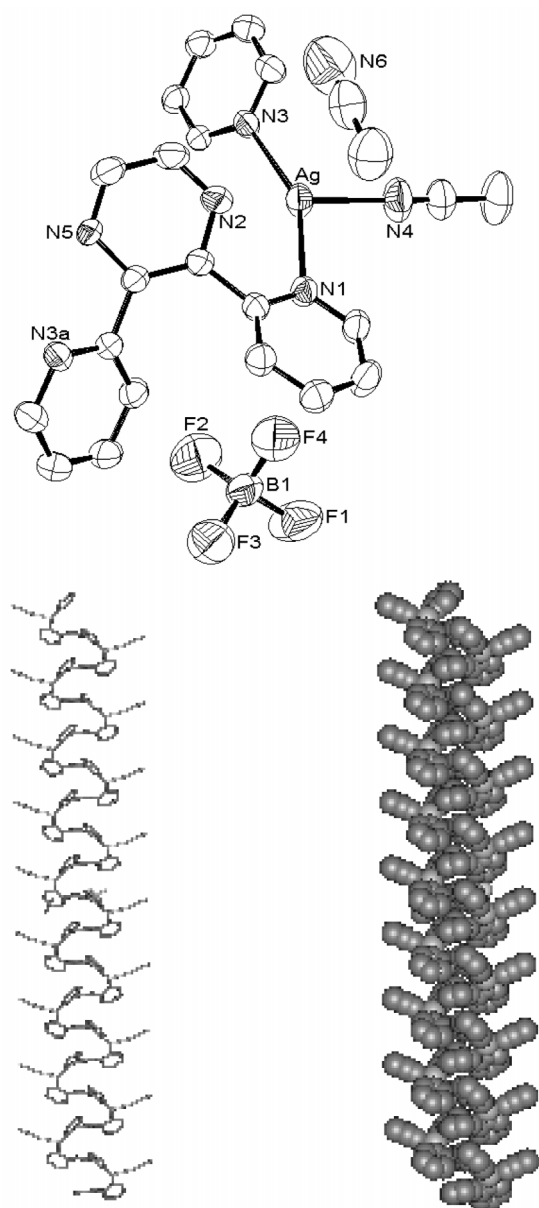


Figure 1. Asymmetric unit (up) and infinite helical structure (left down: stick; left right: space filling) of $[\text{Ag}(\text{bpp})(\text{CH}_3\text{CN})]\text{BF}_4 \cdot \text{CH}_3\text{CN}$. For the infinite helical structure, counteranions and solvate molecules was omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (°) for $[\text{Ag}(\text{bpp})(\text{CH}_3\text{CN})]\text{BF}_4 \cdot \text{CH}_3\text{CN}$

Ag-N(1)	2.368(3)	Ag...N(2)	2.590(4)
Ag-N(3)	2.331(3)	Ag-N(4)	2.283(4)
Ag...N(5)'	2.564(3)		
N(1)-Ag-N(2)	66.3(1)	N(1)-Ag-N(3)	151.8(1)
N(1)-Ag-N(4)	98.2(1)	N(3)-Ag-N(4)	109.7(2)
N(4)-Ag-N(5)'	120.1(2)	N(3)-Ag-N(5)'	68.1(1)
N(1)-Ag-N(5)'	94.4(1)	N(4)-Ag-N(2)	149.9(2)
N(3)-Ag-N(2)	90.2(1)	N(5)-Ag-N(2)	87.8(1)

ion interacts with N(2) and N(5)' (Ag-N(2)...2.590(4) Å; Ag...N(5)', 2.564(3) Å), and thus, may be best described as a pseudo five-coordinate arrangement. Each bpp spacer is linked to the two Ag(I) atoms, resulting in an infinite helix. The helix consists of a single strand of alternating Ag(I) and bpp. There are two units in each turn (2_1 along the b axis), and the helical pitch is 7.731(1) Å. The helices are arrayed in alternate right-handed and left-handed fashion, which is similar to the results of Ciani *et al.*¹² There are two acetonitrile molecules within a crystallographic unit. Interestingly, one acetonitrile molecule is coordinated to the silver(I) metal as a third ligand whereas the other is simply solvated.

Thermal and IR Properties. The traces of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) are shown in Figure 2. The TGA curve shows the weight loss corresponding to the acetonitrile molecules (obs. 12.9%, calc. 16.1%) around 100 °C (eq. 1), and follows by the dissociation of bpp (obs. 45.1%, calc. 45.8%) around 400 °C (eq. 2). The solvate and coordinate acetonitrile molecules could not be discerned by the thermal analysis, showing that the Ag-NCCH₃ is not a strong bond. The erratic value in the first weight loss may be ascribed to the partial evaporation of solvate acetonitrile after the crystals were removed from the mother liquor.

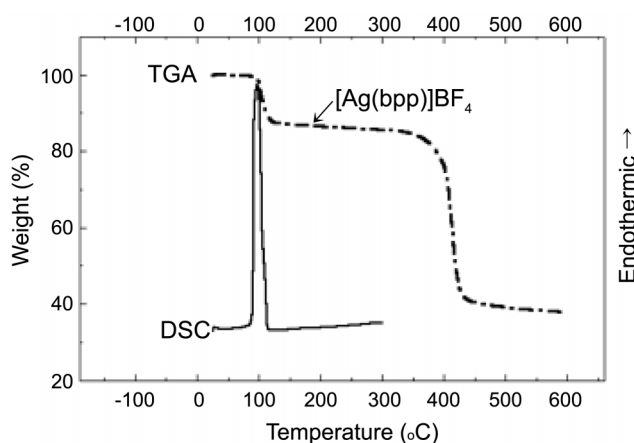
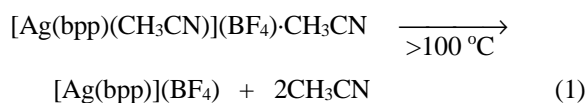


Figure 2. Overlay of TGA and DSC traces of $[\text{Ag}(\text{bpp})(\text{CH}_3\text{CN})]\text{BF}_4 \cdot \text{CH}_3\text{CN}$, each recorded at heating rate of 5 °C min⁻¹.

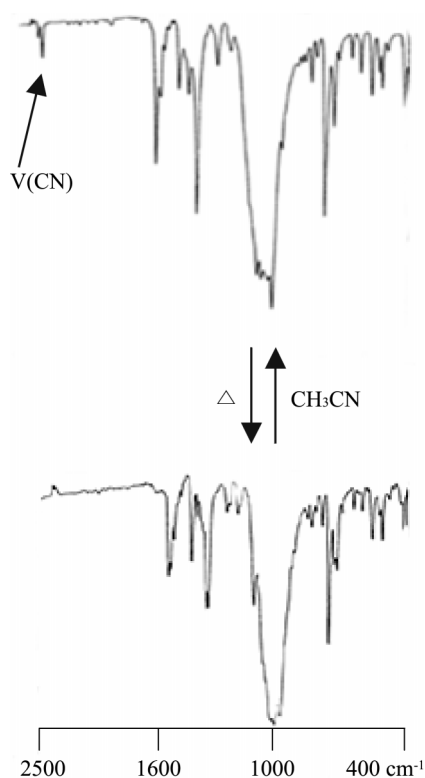
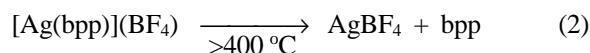


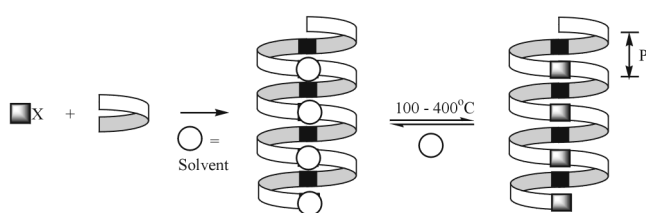
Figure 3. (a) IR (KBr pellet) of as-synthesized, $[\text{Ag}(\text{bpp})(\text{CH}_3\text{CN})]\text{BF}_4 \cdot \text{CH}_3\text{CN}$ (up) and after-calcined (130°C), $[\text{Ag}(\text{bpp})]\text{BF}_4$ (down).



The IR spectra were measured for the complex both as-synthesized and after-calcined at 130°C (Figure 3). The principal bands of the after-calcined sample are very similar to those of the as-synthesized sample except for the disappearance of acetonitrile band, indicating that the acetonitrile molecules are dissociated from the crystal without the collapse of the skeleton at that temperature. The results of IR spectra are consistent with the TGA analysis.

Discussion

Our primary strategy employed is the appropriate combination of a Ag(I) ion with a potential helical spacer. In contrast to cyclodimeric $[\text{Ag}(\text{bpp})]\text{CF}_3\text{CO}_2$ ²⁴ and $[\text{Ag}(\text{bpq})]\text{BF}_4$ (bpq = 2,3-bis(pyridyl)quinoxaline),²² the reaction based on this design strategy results in a self-assembly of a unique helix (Scheme 1). The helix is efficiently constructed irre-



Scheme 1

spective of the reactant stoichiometry, solvent type, and concentration. A key driving force of the helical structure may be ascribed to the intrinsic skewed conformation of the bpp ligand. The nature of an anion is significant for the formation of the helix. For instance, the coordinating nature of CF_3CO_2^- is an obstacle in the construction of the helix. The CF_3CO_2^- analog afforded a discrete cyclodimeric molecule instead of the helical molecule.²⁴ A more weakly donating anion like BF_4^- seems to be favorable for the formation of $[(\text{bpp})\text{Ag}(\text{I})]$ helical species. Thus, the construction of desirable functional molecules may be significantly affected by the delicate difference between counteranions. Of course, the steric effect of a spacer ligand cannot be ignored. For example, the reaction of AgBF_4 with the bulkier bpq ligand afforded a discrete cyclodimeric molecule.²²

On the other hand, a salient feature is that the helical skeleton remains stable without the collapse after the dissociation of the coordinated acetonitriles in the solid state. Furthermore, after the calcined sample is left in acetonitrile, the IR spectrum returns to the spectrum of the as-synthesized sample, disclosing that acetonitrile molecules are reversibly dissociated and associated from the helical structure. The stability of the intermediate, $[\text{Ag}(\text{bpp})](\text{BF}_4)$, in a wide temperature range $100\text{--}400^\circ\text{C}$ may be in part attributed to the stable skeleton without any serious angle strain. Various stable two-coordinate silver(I) complexes have been previously reported from our research group.^{14,15,25}

Conclusions

The bpp ligand is a fascinating helical tectonic unit without any particular strain. The ligating nature of a counteranion may be a crucial hindrance in the formation of a helical structure. Our results clearly demonstrate that the present helical skeleton is very stable against the change in the coordination number. The construction and related properties of molecular helices may contribute to the development of desirable molecular-based materials such as sensors, molecular switches, ion exchangers, chemical delivery, and intercalators.

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Supporting Information Available: Crystallographic data for $[\text{Ag}(\text{bpp})(\text{CH}_3\text{CN})]\text{BF}_4 \cdot \text{CH}_3\text{CN}$. This information is available from OSJ.

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