Molecular Strands and Related Properties of Silver(I) Triflate with 3,3’-Oxybispyridine vs 3,3’-Thiobispyridine

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Studies on subtle spacer ligand effects of AgCF$_3$SO$_3$ with 3,3’-Py$_2$X (X = O vs S) have been carried out. The reaction of AgCF$_3$SO$_3$ with 3,3’-Py$_2$O and 3,3’-Py$_2$S produces [Ag(CF$_3$SO$_3$)(3,3’-Py$_2$O)] and [Ag(3,3’-Py$_2$S)] (CF$_3$SO$_3$), respectively. Crystallographic characterization of [Ag(CF$_3$SO$_3$)](3,3’-Py$_2$O) (monoclinic $Pb1$, $a = 8.405(2)$ Å, $b = 10.714(2)$ Å, $c = 18.031(2)$ Å, $\alpha = 77.36(2)^\circ$, $\beta = 107.83(2)^\circ$, $\gamma = 66.92(2)$, $V = 1438.0(5)$ Å$^3$, $Z = 2$, $R = 0.0498$) reveals that the skeleton structure is an anion-bridged double-strand. The double-strands are packed like a plywood. The framework of [Ag(3,3’-Py$_2$S)](CF$_3$SO$_3$) (orthorhombic $Pcab$, $a = 17.330(2)$ Å, $b = 8.640(1)$ Å, $c = 19.933(6)$ Å, $V = 2985(1)$ Å$^3$, $Z = 8$, $R = 0.0437$) is a sinusoidal single-strand. The formation of each coordination polymer appears to be primarily associated with the donating ability and the conformational energy barrier of the spacer ligands. Thermal analyses indicate that [Ag(CF$_3$SO$_3$)](3,3’-Py$_2$O) and [Ag(3,3’-Py$_2$S)](CF$_3$SO$_3$) are stable up to 250 °C and 210 °C, respectively. For the anion exchangeability, the nature of the spacer ligand is more significant factor than the distance of silver(I)···triflate.

Key words : Strands, Coordination polymers, Silver(I) complexes, Bipyridines, Anion exchange

Introduction

Rational design strategies for functional coordination motifs are now of great interest due to applicable properties such as electrical conductors, molecular magnets, host-guest molecules, crystal bending materials, and nonlinear optical materials. Such desirable coordination polymers have been constructed by selecting the coordination geometry of central metals, the structure of spacer ligands, the nature of counterions, and the reaction condition. In particular, delicate differences between spacer ligands may significantly affect the formation of the coordination polymers. We previously reported that the reaction of Ag(I) with 3,3’-chalcogenobispyridine (3,3’-Py$_2$X; X = O, S) results in the formation of cylindrical helices and that the helices reversibly stretch via counteranion exchange. In 3,3’-Oxybispyridine and 3,3’-thiobispyridine (3,3’-Py$_2$S) as spacer ligands have similar angular and flexible components that possess non-rigid interannular dihedral angles between two pyridyl groups. However, both anions exhibit delicate differences in the size, lone-pair delocalization, and conformational energy barrier, and donating ability.

In order to scrutinize differences in bonding effects between the 3,3’-Py$_2$S and 3,3’-Py$_2$O, we describe the studies on the structures and related properties of Ag(I) CF$_3$SO$_3$ with 3,3’-Py$_2$O vs 3,3’-Py$_2$S. Trifluoromethanesulfonate (CF$_3$SO$_3^-$; triflate) is a common, readily available counter(anion), which coordinates relatively weakly to metal centers. The triflate anion has been known as a weak base and hence as a good leaving group. How can we leverage the structural and chemical differences between 3,3’-Py$_2$O and 3,3’-Py$_2$S to design functional coordination polymers with novel properties?

Materials and Measurements

Silver(I) triflate (AgCF$_3$SO$_3$) was purchased from Aldrich Chemical Co, and used without further purification. 3,3’-Py$_2$O and 3,3’-Py$_2$S were prepared according to the literature procedures. Elemental analyses (C, H, N) were performed on crystalline samples by the Advanced Analytical Center at KIST with a Perkin-Elmer 2400 CHNS Analyzer. Thermal analyses were carried out under dinitrogen atmosphere at a scan rate of 10 °C/min with a Stanton Red Croft TG 100. X-ray powder diffraction data were recorded on a Rigaku RINT/DMAX-2500 diffractometer at 40 kV, 126 mA for Cu Kα. Infrared spectra were obtained on a Perkin Elmer 16P FTIR spectrophotometer with samples prepared as KBr pellet.

Preparation of [Ag(CF$_3$SO$_3$)(3,3’-Py$_2$O)]. A methanol solution (5 mL) of 3,3’-Py$_2$O (65 mg, 0.3 mmol) was slowly diffused into an aqueous solution (5 mL) of AgCF$_3$SO$_3$ (77 mg, 0.3 mmol). Colorless crystals of [Ag(CF$_3$SO$_3$)(3,3’-Py$_2$O)] suitable for crystallographic characterization formed at the interface, and were obtained in 7 days in 83% yield. Mp: 250-251 °C (dec). Found: C, 30.60; H, 1.83; N, 6.38. Anal. Calc'd for C$_{18}$H$_{17}$AgF$_3$O$_4$S: C, 30.79; H, 1.88; N, 6.58. IR (KBr, cm$^{-1}$): ν(SO$_3^-$), 1264(s).

Preparation of [Ag(3,3’-Py$_2$S)](CF$_3$SO$_3$). The diffusion of a methanol solution (6 mL) of 3,3’-Py$_2$S (60 mg, 0.3...
Scheme 1

**Molecular Strands of Ag(I) Complexes**

**Results and Discussion**

The reaction of AgCF$_3$SO$_3$ with 3,3′-Py$_2$O and 3,3′-Py$_2$S in appropriate solvents affords [Ag(CF$_3$SO$_3$)(3,3′-Py$_2$O)] and [Ag(3,3′-Py$_2$S)(CF$_3$SO$_3$)], respectively (Scheme 1). Elemental analyses confirm that both products are 1 : 1 (Ag : Py$_2$X (X = O, S)) adducts. The molecular formulae of the two compounds are very similar, but their infinite structures are basically different, which will be explained in detail. The reactions are independent of the variation of the mole ratio, reaction time, and concentration, indicating that the products are favorable species. Moreover, when acetone or ethanol was used as a solvent instead of methanol, the same products were obtained. The compounds are insoluble in water and common organic solvents, but are stable for several days at pH = 3.5–9.0 aqueous suspensions.

**Crystal Structures.** The crystallographic asymmetric unit and extended structures of [Ag(CF$_3$SO$_3$)(Py$_2$O)] are shown in Figure 1, and selected bond lengths and angles are listed in Table 2. There are two independent silver units in the asymmetric region of the triclinic unit cell and the features of the two molecules are within error of being identical. The Py$_2$O spacer connects two silver ions to give a single strand (Ag-N = 2.173(5)-2.196(5) Å). The two single strands are double-bridged via one oxygen atom of the triflate anion in “up and down” to give double strand (Ag-O = 2.555(6)-2.577(5) Å), resulting in the approximately four-coordinate Ag(I) ion. The Ag-O distances are comparable to the corresponding bond in [Ag(NO$_3$)$_2$(Py$_2$)$_2$H$_2$O]. The dihedral angles between two pyridine rings around O and Ag are 80.5(2)-80.6(2)°. A salient feature is that the double strands are packed like a plywood.

The asymmetric unit and infinite structures of [Ag(Py$_2$S)]

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**Table 1. X-ray Crystal Data and Details of Data Collections and Structure Refinements**

<table>
<thead>
<tr>
<th></th>
<th>[Ag(CF$_3$SO$_3$)]</th>
<th>[Ag(3,3′-Py$_2$S)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C$<em>{11}$H$</em>{8}$N$<em>{2}$AgO$</em>{4}$</td>
<td>C$<em>{11}$H$</em>{8}$N$<em>{2}$AgF$</em>{3}$O$<em>{3}$S$</em>{2}$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>429.13</td>
<td>445.19</td>
</tr>
<tr>
<td>Space group</td>
<td>$P\bar{T}$</td>
<td>$P\bar{c}ab$</td>
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<tr>
<td>$a$ (Å)</td>
<td>8.405(2)</td>
<td>17.330(2)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>10.714(2)</td>
<td>8.640(1)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>18.031(2)</td>
<td>19.933(6)</td>
</tr>
<tr>
<td>$\alpha$ (°)</td>
<td>77.36(2)</td>
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</tr>
<tr>
<td>$\beta$ (°)</td>
<td>76.56(2)</td>
<td></td>
</tr>
<tr>
<td>$\gamma$ (°)</td>
<td>66.92(2)</td>
<td></td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>1438.0(5)</td>
<td>2984.6(1)</td>
</tr>
<tr>
<td>$Z$</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>$D_{cal}$ (gcm$^{-3}$)</td>
<td>1.982</td>
<td>1.981</td>
</tr>
<tr>
<td>$\mu$, mm$^{-1}$</td>
<td>1.599</td>
<td>1.674</td>
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<tr>
<td>Goodness-of-fit on $R^2$</td>
<td>1.102</td>
<td>1.105</td>
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<tr>
<td>$R$ [$\sigma(2\sigma)$]</td>
<td>0.0486</td>
<td>0.0437</td>
</tr>
<tr>
<td>$wR$</td>
<td>0.1264</td>
<td>0.1234</td>
</tr>
</tbody>
</table>

$R1 = \sum||F_o|| - |F_c||/\sum|F_o||$, $wR2 = \sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2$, where $w = 1/[\sigma(F_o^2 + (aP)^2 + bP)]$, where $P = (\text{Max}(F_o^2, 0)) + 2F_c^2)/3$
(CF$_3$SO$_3$) are shown in Figure 2, and selected bond lengths and angles are listed in Table 2. Each Py$_2$S ligand connects two silver(I) ions in a bridged fashion to give a single strand. The Ag-N bonds (2.172(5) Å and 2.167(5) Å) are not exceptional. The shortest distance of Ag⋯O (CF$_3$SO$_3$) (2.80 Å) is much longer than the corresponding length of [Ag(CF$_3$SO$_3$)(Py$_2$O)]. However, the weak interaction is a partial responsibility for the ideal linear geometry (N(1)-Ag-N(2) = 157.5(2)°). The packing diagram indicates that the single strand is a sinusoidal chain that is arrayed in alternate sin(α) and cos(α) fashion. The dihedral angle between two pyridine rings within the Py$_2$S ligand is 74.4(2)° while the dihedral angle around Ag(I) ion is 34.1(3)°. The Py-S-Py angle (101.4(3)°) is much smaller than the corresponding angle Py-O-Py (116.1(5)°; 116.0(5)°) of [Ag(CF$_3$SO$_3$)(Py$_2$O)].

**Thermal Analyses.** The thermal analyses have been used to establish a relationship between structure and properties. The traces of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) indicate that [Ag(CF$_3$SO$_3$)(Py$_2$O)] and [Ag(Py$_2$S)](CF$_3$SO$_3$) are thermally stable up to 250 and 213 °C, respectively, in the solid state (Figure 3). [Ag(CF$_3$SO$_3$)(Py$_2$O)] shows a two-step weight loss in the temperature range 250-403 °C and [Ag(Py$_2$S)](CF$_3$SO$_3$) exhibits a similar thermal pattern in the range 213-410 °C. The two-step weight loss may be ascribed to the evaporation of the spacer and the anion. The thermal curves suggest that the anion-bridged double-strand, [Ag(CF$_3$SO$_3$)(Py$_2$O)], is more stable than the sinusoidal single-strand, [Ag(Py$_2$S)](CF$_3$SO$_3$).

### Table 2. Selected Bond Lengths (Å) and Bond Angles (°)

<table>
<thead>
<tr>
<th></th>
<th>[Ag(CF$_3$SO$_3$) (3,3′-Py$_2$O)]</th>
<th><a href="CF$_3$SO$_3$">Ag(3,3′-Py$_2$S)</a></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(1)-N(2)</td>
<td>2.174(5)</td>
<td>2.167(5)</td>
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<td>Ag(1)-N(1)</td>
<td>2.196(5)</td>
<td>2.172(5)</td>
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<td>Ag(1)-O(8)#1</td>
<td>2.560(6)</td>
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<tr>
<td>Ag(1)-O(8)</td>
<td>2.577(5)</td>
<td></td>
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<tr>
<td>Ag(2)-N(4)</td>
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<tr>
<td>Ag(2)-N(3)</td>
<td>2.195(5)</td>
<td></td>
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<tr>
<td>Ag(2)-O(3)#2</td>
<td>2.555(6)</td>
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<tr>
<td>Ag(2)-O(3)</td>
<td>2.575(5)</td>
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<tr>
<td>O(3)-Ag(2)#2</td>
<td>2.555(6)</td>
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<tr>
<td>O(8)-Ag(1)#1</td>
<td>2.560(6)</td>
<td></td>
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<tr>
<td>N(2)-Ag(1)-N(1)</td>
<td>156.9(2)</td>
<td>157.5(2)</td>
</tr>
<tr>
<td>N(2)-Ag(1)-O(8)#1</td>
<td>110.2(2)</td>
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<tr>
<td>N(1)-Ag(1)-O(8)#1</td>
<td>92.0(2)</td>
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<td>N(2)-Ag(1)-O(8)</td>
<td>99.5(2)</td>
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<td>N(1)-Ag(1)-O(8)</td>
<td>91.9(2)</td>
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<td>O(8)#1-Ag(1)-O(8)</td>
<td>75.1(2)</td>
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<td>N(4)-Ag(2)-N(3)</td>
<td>156.9(2)</td>
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<td>110.1(2)</td>
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<td>N(3)-Ag(2)-O(3)#2</td>
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<td>N(4)-Ag(2)-O(3)</td>
<td>99.7(2)</td>
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<td>N(3)-Ag(2)-O(3)</td>
<td>92.0(2)</td>
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<tr>
<td>O(3)#2-Ag(2)-O(3)</td>
<td>74.8(2)</td>
<td></td>
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</tbody>
</table>

For [Ag(3,3′-Py$_2$S)](CF$_3$SO$_3$), symmetry transformations used to generate equivalent atoms: #1 x, -y-1/2, z-1/2; #2 x, -y-1/2, z+1/2.
Anion Exchange. For the present compounds, a typical anion exchange can occur since the triflate is a good leaving group. The anion exchange of [Ag(CF$_3$SO$_3$)(Py$_2$O)] with X$^-$ (X$^-$ = BF$_4^-$, ClO$_4^-$, and PF$_6^-$) was accomplished in a typical aqueous media. To investigate the exchange procedure, the anion exchange was monitored by the characteristic IR bands of the anions.$^{23,24}$ The infrared spectra show the gradual disappearance of intense CF$_3$SO$_3^-$ bands (1264 cm$^{-1}$) and the appearance and growth of new anion bands (1058 cm$^{-1}$ for BF$_4^-$; 1090 cm$^{-1}$ for ClO$_4^-$; 836 cm$^{-1}$ for PF$_6^-$). The anion exchanges were completed within 12 h (Figure 4). The elemental analysis and IR spectra of the exchanged species are coincident with those of the as-synthesized samples.$^{23,24}$

We expected that the anion of [Ag(Py$_2$S)(CF$_3$SO$_3$)] could be more easily exchanged since the anion is more labile. However, the anion exchange of [Ag(Py$_2$S)(CF$_3$SO$_3$)] is slower than that of [Ag(CF$_3$SO$_3$)(Py$_2$O)]. The anions of [Ag(Py$_2$S)(CF$_3$SO$_3$)] were not completely exchanged after 24 h. The anion exchangeability of these compounds seems to be governed by the nature of the spacer ligand rather than the distance of Ag(I)--CF$_3$SO$_3$. The hydrophilicity-difference between the two spacer ligands may play an important role in the anion exchange. Such an interconversion via the anion exchange may be applied to the development of a tailored strategy that cannot be approached by direct synthetic methods.

Construction of Each Molecular Strand. Py$_2$O and Py$_2$S are similar noninnocent ligands that possess stable skewed conformers with nonrigid interannular dihedral angles between two pyridyl groups. The reaction of Ag(I)CF$_3$SO$_3$ with 3,3'-Py$_2$O affords a plywood structure consisting of double strands while the treatment of Ag(I)CF$_3$SO$_3$ with 3,3'-Py$_2$S produces a sinusoidal single strand. The formation of each structure may be ascribed to the intrinsic properties of the spacer ligands. There are delicate differences between the two spacers in the size, the bond angle, the lone-pair delocalization of chalcogens, the conformational energy barrier, and the donating ability of nitrogen atoms. First, the C-S-C angle of 3,3'-Py$_2$S was smaller than the C-O-C angle of 3,3'-Py$_2$O.$^{23}$ For the present works, the C-S-C angle (101.4(3)°) significantly contracts relative to the corresponding C-O-C angle in 3,3'-Py$_2$O (116.1(6)°). The contracted angle of the bridged-bidentate spacer may be an obstacle in the formation of higher coordination number. Therefore, the 3,3'-Py$_2$S spacer may afford the simple two-coordinate sinusoidal structure in contrast to the four-coordinate double strand. Second, the conformational energy barrier of 3,3'-Py$_2$S is slightly different from that of 3,3'-Py$_2$O.$^{31,32}$ The low energy barrier seems to be an unfavorable factor in the formation of crowded coordination. Third, the coordination numbers of each Ag(I) ion may be induced by the donating ability of the spacer ligands. The Ag-N bond lengths of [Ag(Py$_2$S)] (CF$_3$SO$_3$) are slightly shorter than those of [Ag(CF$_3$SO$_3$)] (Py$_2$O). Furthermore, [Ag(CF$_3$SO$_3$)(Py$_2$O)] is four-coordinate Ag(I) whereas [Ag(Py$_2$S)](CF$_3$SO$_3$) approximates to two-coordinate Ag(I). These facts indicate that the Lewis basicity of 3,3'-Py$_2$S is stronger than that of 3,3'-Py$_2$O.

In conclusion, the 3,3'-Py$_2$X spacers are a series of fascinating tectonic units without any serious strain in the formation of various coordination polymers. A direct comparison between 3,3'-Py$_2$S and 3,3'-Py$_2$O demonstrates that the delicate difference in intrinsic nature acts as a crucial factor in the construction of molecular materials. In particular, exchangeable triflate is useful in generating new species that cannot be approached by direct synthetic methods.

Figure 3. Overlay of TGA (--) and DSC (--) traces of [Ag(3,3'-Py$_2$O)(CF$_3$SO$_3$)] (a) and [Ag(3,3'-Py$_2$S)(CF$_3$SO$_3$)] (b), each recorded at a heating rate of 10°C min$^{-1}$.

Figure 4. IR spectra of [Ag(3,3'-Py$_2$O)(CF$_3$SO$_3$)] (a), species exchanged by BF$_4^-$ (b), ClO$_4^-$ (c), and PF$_6^-$ (d). *denotes the bands induced by each anion.
methods. For the present works, the anion exchangeability is strongly dependent upon the nature of a spacer ligand rather than the distance of silver(I)···triflate. The delicate differences may contribute to the development of useful molecular-based materials.

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References