

Properties of *N,N*-Bis[2-(isonicotinoyloxy)ethyl]-*p*-toluenesulfonamide. Structures of Its Silver(I) Complexes *via* Anion Effects

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N,N-Bis[2-(isonicotinoyloxy)ethyl]-*p*-toluenesulfonamide (**L**) as a new ligand was synthesized and characterized. The photoluminescence spectrum of **L** shows a bright blue emission at 417 nm. The slow diffusion of an organic solution of **L** into an aqueous solution of AgX (X = BF₄⁻ and ClO₄⁻) affords a metallacyclodimer consisting of [Ag(**L**)₂X₂]. Each **L** acts as a bidentate fashion, and thus connects two Ag(I) ions to form the metallacyclodimer. For [Ag(**L**)₂(BF₄)₂], the BF₄⁻ anions are positioned around Ag(I) ion, and for [Ag(**L**)₂(ClO₄)₂], the ClO₄⁻ anions are positioned at the metallacyclodimeric ring. The delicate difference between both structures in solid state can be explained by the coordinating ability of anions.

Key Words : Anion effects, *N,N*-Bis[2-(isonicotinoyloxy)ethyl]-*p*-toluenesulfonamide, Crystal structures, Metallacyclodimers, Silver(I) complexes

Introduction

The control of macrocyclic rings by means of external perturbation is a hot issue in the construction of molecular machines as well as aesthetic molecules.¹⁻⁵ In particular, various metallamacrocycles have been studied as important building blocks in the construction of functional supramolecular materials that can be utilized for molecular recognition, selective transformation, drug delivery systems, catalysts, storage, and biomimics.⁶⁻²⁰ Facile synthetic methods are either the ring-expansion²¹⁻²³ by means of labile metal-ligand coordination or the ring-formation *via* appropriate tectonics.^{13,16-20} Among various metallamacrocycles, silver(I) complexes of multidentate N-donor ligands have contributed to the synthesis of metal coordination materials such as catalysts,²⁴ rectangle building blocks,^{13,16} and task-specific topology.²⁵ Tuning of molecular topology of polypyridyl spacers *via* the balance of steric and inductive effects is a very important field in metallacyclic supramolecular chemistry.¹⁶ Such polypyridyl ligands that can bridge two or more remote metal centers have been utilized in the synthesis of abiotic functional supramolecules that exhibit mixed valence, anion exchange, photoinduced electron or energy transfer, sensing, polymorphism, and magnetic exchange between paramagnetic centers.²⁶⁻³¹ Thus, delicate design and synthesis of new tectonics is one of the most important tasks in the field of construction of functional metallacycles. Of the N-donor ligands, some (iso)nicotinoyl-containing spacers have served as appropriate building blocks for various supramolecular materials.^{32,33} The (iso)nicotinoyl-containing spacers possess characteristic properties such as a potential multidentate, an *sp*² angle around C=O (~120°), a malleable length, conformational nonrigidity, and manageable solubility.

In an effort to investigate the coordination chemistry of new *N,N*-bis[2-(isonicotinoyloxy)ethyl]-*p*-toluenesulfon-

amide ligand, the reaction of AgX (X = ClO₄⁻ and BF₄⁻; very similar in both volume and geometry) with the ligand was carried out. We report the properties of the new ligand, and delicate structures of its silver complexes *via* anion effects.

Experimental

Materials and Measurements. AgX salts (X⁻ = BF₄⁻ and ClO₄⁻) were purchased from Aldrich Chemicals, and used without further purification. Elemental microanalyses (C, H, N) were performed on crystalline samples by the Pusan Center at KBSI using a Perkin Elmer 2400 CHN analyzer. ¹H NMR spectra were recorded on a Varian Mercury Plus 300 operating at 300.00 MHz, and the chemical shifts were relative to the internal Me₄Si. Thermal analyses were carried out under a dinitrogen atmosphere at a scan rate of 10 °C/min using a Stanton Red Croft TG 100. Infrared spectra were obtained on a Nicolet 380 FTIR spectrophotometer with samples prepared as KBr pellets. The ultraviolet and photoluminescence (PL) spectra were measured using a Jasco V-570 UV-vis spectrometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively.

Synthesis of *N,N*-Bis[2-(isonicotinoyloxy)ethyl]-*p*-toluenesulfonamide (L**).** Pyridine (19.41 mL, 0.24 mol) was added to a solution of isonicotinoyl chloride hydrochloride (21.36 g, 0.12 mol) in chloroform (150 mL) at room temperature. Subsequently, *N,N*-bis(2-hydroxyethyl)-*p*-toluenesulfonamide (12.966 g, 0.05 mol) was added to the reaction solution, and the mixture was refluxed for 24 h. The chloroform layer was washed successively with 0.5 N NaOH solution and cold water. The chloroform solution was dried using magnesium sulfate and filtered. Removal of the solvent gave *N,N*-bis[2-(isonicotinoyloxy)ethyl]-*p*-toluenesulfonamide (**L**). The product was obtained as crystalline

solids in 83% yield. Mp. 93 °C. ^1H NMR (300 MHz, CDCl_3 , Me_4Si): = 8.72 (d, $J = 5.4$ Hz, 1H), 7.73 (d, $J = 5.8$ Hz, 1H), 7.67 (d, $J = 8.1$ Hz, 1H), 7.21 (d, $J = 8.4$ Hz, 1H), 4.51 ($J = 5.7$ Hz, 2H), 3.61 (t, $J = 5.7$ Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (CDCl_3 , Me_4Si): = 164.835, 150.691, 143.967, 136.785, 136.136, 130.039, 127.156, 122.868, 63.453, 47.738, 21.532. IR (KBr, cm^{-1}): 1726 (ν_{CO}).

[Ag(L)]₂(BF₄)₂. A dichloromethane solution of **L** was slowly diffused into a methanol solution of AgBF_4 in the mole ratio of 1:1. Yield: 65% based on Ag(I) salt. Calcd (found) for $\text{C}_{16}\text{H}_{16}\text{Ag}_2\text{B}_2\text{F}_8\text{N}_6\text{O}_{12}\text{S}_2$: C, 41.60 (41.20), H, 3.49 (3.38), N, 6.33 (6.20). IR (KBr, cm^{-1}): $\nu(\text{BF}_4)$, 1054 (s).

[Ag(L)]₂(ClO₄)₂. The complex was prepared as the similar procedure as $[\text{Ag(L)}]_2(\text{BF}_4)_2$. A dichloromethane solution of **L** was slowly diffused into a methanol solution of AgClO_4 in the mole ratio of 1:1. Yield: 70% based on Ag(I) salt. Calcd (found) for $\text{C}_{16}\text{H}_{16}\text{Ag}_2\text{Cl}_2\text{N}_6\text{O}_{20}\text{S}_2$: C, 40.82 (39.90), H, 3.43 (3.42), N, 6.21 (6.12). IR (KBr, cm^{-1}): $\nu(\text{ClO}_4)$, 1088 (s).

X-ray Crystallography. All X-ray data were collected on a Bruker SMART automatic diffractometer with a graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073$ Å) and a CCD detector at ambient temperature. The 45 frames of two dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The data were corrected for Lorentz and polarization effects. Absorption effects were corrected by the empirical ψ -scan method. The structures were solved by the direct method (SHELXS 97) and refined by full-matrix least squares techniques (SHELXL 97).³⁴ The non-hydrogen 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 are given in Table 1.

Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (CCDC-699166 and 699167). The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/perl/catreq/catreq.cgi> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1233 336033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

Synthesis and Properties of Ligand. Reaction of *N,N*-bis(2-hydroxyethyl)-*p*-toluenesulfonamide with isonicotinoyl chloride hydrochloride in chloroform smoothly produces the new ligand (**L**) as depicted in Scheme 1. Its composition and structure were confirmed by chemical analysis, IR, ^1H NMR, thermal analysis, and ^{13}C NMR. The crystalline product is soluble in *N,N*-dimethylformamide, dimethylsulfoxide, chloroform, and dichloromethane, but is insoluble in hexane and water. The ligand sharply melts at 95 °C, and begins to decompose at 292 °C (Figure 1). The decomposed volatiles are drastically evaporated around 300 °C. The photoluminescence spectrum shows that **L** is a bright blue emitting material with a peak at 417 nm. The emission spectrum of **L** was measured in acetone (Figure 2). The solid compound also shows the blue color under the UV light as depicted in inset in the figure. About 90% of the luminescence appears at the blue region below 500 nm, and thus **L** is a very promising candidate for a blue phosphorescent material. The blue luminescence seems to be originated from the change of π - π^* transition in contrast to the starting material, *N,N*-bis(2-hydroxyethyl)-*p*-toluenesulfonamide,

Table 1. Crystallographic Data

	$[\text{Ag(L)}]_2(\text{BF}_4)_2$	$[\text{Ag(L)}]_2(\text{ClO}_4)_2$
Empirical formula	$\text{C}_{23}\text{H}_{23}\text{AgBF}_4\text{N}_3\text{O}_6\text{S}$	$\text{C}_{23}\text{H}_{23}\text{AgClN}_3\text{O}_{16}\text{S}$
Formula weight	664.18	676.82
Wavelength	0.71073 Å	0.71073 Å
Crystalsystem	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions	a = 7.8231(6) Å b = 9.9521(7) Å c = 32.943(2) Å $\beta = 94.4200(10)^\circ$	a = 7.8157(7) Å b = 10.0585(9) Å c = 33.015(3) Å $\beta = 94.060(2)^\circ$
V	2557.2(3) Å ³	2588.9(4) Å ³
Z	4	4
D (calculated)	1.725 Mg/m ³	1.736 Mg/m ³
Absorption coefficient	0.944 mm ⁻¹	1.025 mm ⁻¹
F(000)	1336	1368
Crystal size	0.20 × 0.20 × 0.15 mm ³	0.20 × 0.10 × 0.10 mm ³
Reflections collected	15716	16201
Data / restraints / parameters	5983 / 0 / 353	6084 / 0 / 353
Goodness-of-fit on F^2	1.320	1.050
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.1670$, $wR2 = 0.3104$	$R1 = 0.0977$, $wR2 = 0.1792$
R indices (all data)	$R1 = 0.2180$, $wR2 = 0.3328$	$R1 = 0.2015$, $wR2 = 0.2225$
Largest diff. peak and hole	1.904 and -2.085 e.Å ⁻³	1.024 and -0.993 e.Å ⁻³

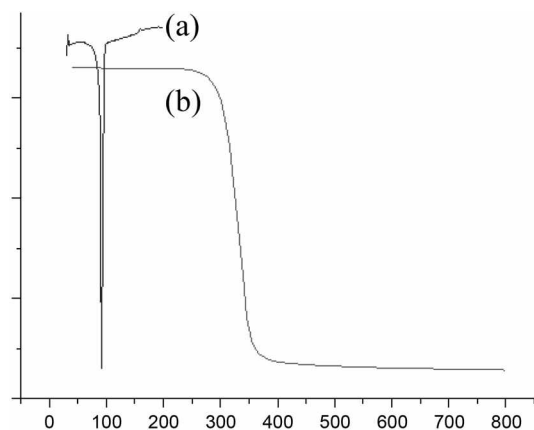
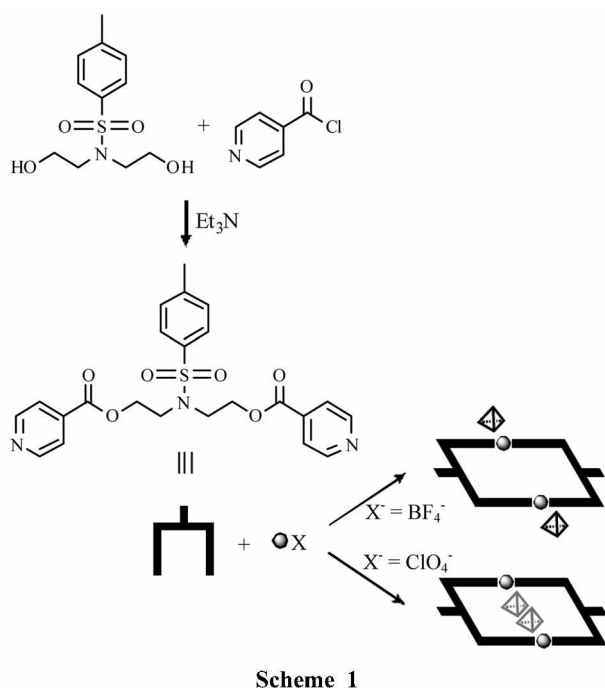


Figure 1. DSC (a) and TGA (b) of **L**.

which did not show the blue luminescence.

Synthesis of Silver(I) Complexes. The slow diffusion of AgX ($\text{X}^- = \text{BF}_4^-$ and ClO_4^-) in methanol with a potential multidentate **L** in dichloromethane produced colorless single crystals suitable for X-ray crystallography (Scheme 1). The reaction was initially carried out at the mole ratio of 1:1, but the same compounds were obtained irrespective of the mole ratio within the range of $\text{L}/\text{M} = 0.5\text{--}2.5$. That is, the formation of the products was not significantly affected by the change of reactant mole ratio and concentration, indicating the compounds are favorable and thermodynamically stable species. The silver complexes are insoluble in common organic solvents, but the Ag(I)-N bonds are dissociated in polar organic solvents such as dimethyl sulfoxide, *N,N*-dimethylformamide, and acetonitrile. The products are air-stable, but slowly turn to gray powder under light.

Crystal Structures. Slow diffusion of AgX with **L** afforded discrete silver(I) complexes in contrast to the formation of coordination polymers of general bipyridyl analogs. X-

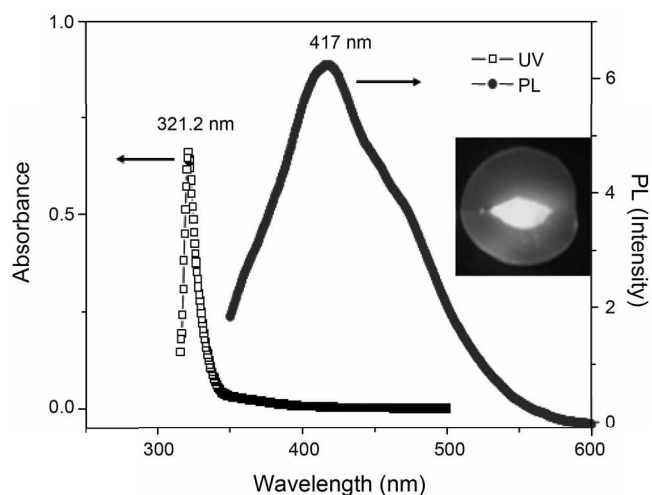


Figure 2. UV and PL spectra of **L**.

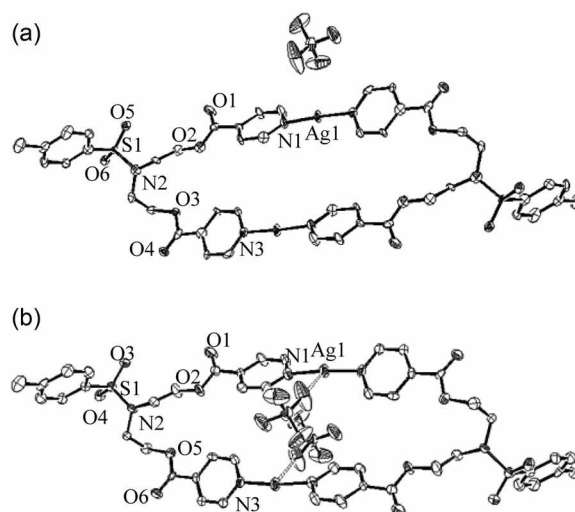


Figure 3. ORTEP drawings of $[\text{Ag}(\text{L})_2(\text{BF}_4)_2]$ (a) and $[\text{Ag}(\text{L})_2(\text{ClO}_4)_2]$ (b). Hydrogen atoms are omitted for clarity. Relevant bond lengths (\AA) and angles ($^\circ$) of $[\text{Ag}(\text{L})_2(\text{BF}_4)_2]$: $\text{Ag}(1)\text{-N}(1) = 2.124(11)$, $\text{Ag}(1)\text{-N}(3') = 2.152(12)$, $\text{N}(1)\text{-Ag}(1)\text{-N}(3') = 175.8(5)$. $[\text{Ag}(\text{L})_2(\text{ClO}_4)_2]$: $\text{Ag}(1)\text{-N}(1) = 2.148(7)$, $\text{Ag}(1)\text{-N}(3') = 2.152(7)$, $\text{Ag}(1)\cdots\text{O}(7) = 2.717$, $\text{N}(1)\text{-Ag}(1)\text{-N}(3') = 175.5(3)$, $\text{N}(1)\text{-Ag}(1)\cdots\text{O}(7) = 95.00$, $\text{O}(7)\cdots\text{Ag}(1)\text{-N}(3') = 81.93$.

ray characterizations on single crystals have provided that the products are metallacyclodimeric species consisting of $[\text{Ag}(\text{L})_2\text{X}_2]$ ($\text{X}^- = \text{BF}_4^-$ and ClO_4^-) (Figure 3). For both complexes, **L** connects two Ag(I) ions ($\text{Ag-N} = 2.12(1)\text{--}2.15(1)$ \AA for $[\text{Ag}(\text{L})_2(\text{BF}_4)_2]$; $\text{Ag-N} = 2.148(7)\text{--}2.152(7)$ \AA for $[\text{Ag}(\text{L})_2(\text{ClO}_4)_2]$) to form a 36-membered metallacyclodimer with two free toluenesulfonamide groups. That is, potential multidentate **L** acts as a typical bidentate fashion. The structure of $[\text{Ag}(\text{L})_2(\text{ClO}_4)_2]$ is basically similar to that of $[\text{Ag}(\text{L})_2(\text{BF}_4)_2]$, but the slight difference between two anions gives different packings ($\text{Ag}\cdots\text{X} = 2.876$ \AA for $[\text{Ag}(\text{L})_2(\text{BF}_4)_2]$; 2.718 \AA for $[\text{Ag}(\text{L})_2(\text{ClO}_4)_2]$). Interestingly, the ClO_4^- anions more closely interact with two Ag(I) ions compared to BF_4^- anions depending on the coordinating ability of the anions. The geometry around the Ag(I) ion of

$[\text{Ag}(\text{L})_2(\text{BF}_4)_2]$ approximates a typical linear arrangement ($\text{N}-\text{Ag}-\text{N} = 175.8(5)^\circ$), and the geometry around the $\text{Ag}(\text{I})$ ion of $[\text{Ag}(\text{L})_2(\text{ClO}_4)_2]$ may be best described as T-shape ($\text{N}-\text{Ag}-\text{N} = 175.5(3)^\circ$; $\text{N}(1)-\text{Ag}(1)\cdots\text{O}(7) = 95.00^\circ$, $\text{O}(7)\cdots\text{Ag}(1)-\text{N}(3) = 81.93^\circ$). Thus, For $[\text{Ag}(\text{L})_2(\text{BF}_4)_2]$, the BF_4^- anions are positioned around $\text{Ag}(\text{I})$ ion, and for $[\text{Ag}(\text{L})_2(\text{ClO}_4)_2]$, the ClO_4^- anions are positioned at the metallacyclodimeric ring. Thus, a keen competition exists between the $\text{Ag}\cdots\text{X}$ and the packing diagram. The coordinating ability of two anions is well coincident with our previous order.³⁵

Construction Principle and Related Properties. The skeleton of both complexes is a discrete metallacyclodimer, but their anion-position is strongly dependent on the nature of the anions. The formation of a metallacyclodimer may be attributed to a suitable combination of the conformer of **L** and the potential linear geometry around the $\text{N}-\text{Ag}-\text{N}$ bonds. In particular, the complexes are exclusively constructed irrespective of the mole ratio of the reactants, the solvent types, and the concentrations.

The position and interaction of anions may be explained by the coordinating nature of anions. The BF_4^- anion has been considered as "non-coordinating" anions compared to ClO_4^- anion.³⁵ According to our previous results, both anions are very similar in geometry and size.²⁵ Thus, the packing of the present products appears to be delicately associated with the coordinating nature of anions rather than size effects of anions. The formation of stable $\text{Ag}-\text{N}$ bonds and $\text{Ag}\cdots\text{X}$ interactions may be partly indebted to the electronic effects of the ligand. For the silver(I) complexes, the blue emission properties were quenched, presumably owing to the change of conformation and electronic effects.

Conclusion

The new blue emitting multidentate bipyridine spacer is a fascinating tectonic in the construction of a discrete cyclodimeric skeleton without any particular strain. The anion-position of the present silver(I) complexes is a good example that the coordinating ability of anions is a very important factor for the molecular packing. The results may contribute to the development of rational bulk materials of coordination complexes.

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