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Silver(I) Complexes of 2,2';6',4''-Terpyridine: The Formation of Discrete Dimers versus Helical Polymers is Anion Dependent

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The ligand 2,2';6',4''-terpyridine combines a chelating bipyridine group and terminal pyridine donor into a single molecule which is incapable of bonding all three donor N-atoms to a single metal center. Upon chelation to Ag(I), a pro-chiral, building block is produced which can subsequently aggregate by terminal coordination of the pyridine nitrogen. Two forms are possible; a discrete bimetallic complex with a center of symmetry and an infinite helical coordination polymer. Which of these structures occurs is dependent upon the counter anion.

Keywords: Nitrogen ligands; Self-assembly; Coordination polymer; Helicate

INTRODUCTION

In metallosupramolecular chemistry, the self-assembly process between metal and ligand is driven by the enthalpic need to saturate both the coordination sphere of the metal ion and the donor capacity of the ligand. Depending upon the structural design of the ligand and the relative orientations of the donor groups, particular metal-ligand species can be targeted. Most often this strategy produces discrete molecular species such as monomers, dimers or larger aggregates with no left-over binding sites or donor atoms as the thermodynamic product. There is always, however, a competing reaction which leads to polymerization; the kinetic product. In this case, saturation is not reached since terminal groups of the polymer are not bonded. Whether one is designing a discrete molecular polygon or trying to create polymers via coordination chemistry, one of the fundamental questions to consider is; *what controls the formation of infinite chains (polymers) versus simple rings (clusters)?* [1–3].

Herein, we report an example of a metal-ligand system in which the balance between two possible structural outcomes is so subtle it appears to be dependent solely on the nature of the counter ion (Fig. 1).

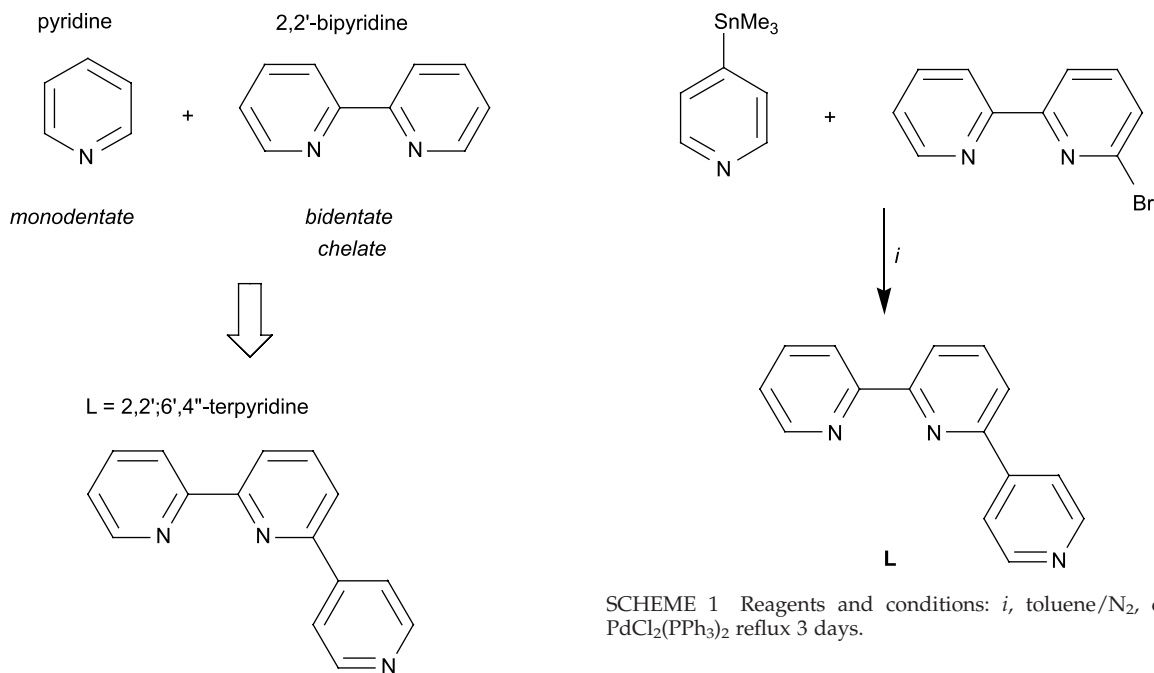
The tridentate ligand 2,2';6',4''-terpyridine, L, combines the chelating ability of 2,2'-bipyridine and the terminal coordination of a simple pyridine into a single molecule. The juxtaposition of the two donor groups is such that binding of all three nitrogen atoms to a single metal is impossible. Chelation to one metal and external coordination to a second metal would therefore be the preferred mode of coordination encouraging the formation of some type of aggregate; ring vs. chain-cluster vs. polymer.

RESULTS AND DISCUSSIONS

The ligand 2,2';6',4''-terpyridine, L was first reported by Constable [4] for use as a cyclometallating analog of the well-known tridentate chelate 2,2':6',2''-terpyridine (terpy). The original preparation employed a Potts' synthesis [5], to produce 4'-thiomethyl-2,2':6',4''-terpyridine which was subsequently reduced to afford L in 31% overall yield. We found that by using the Stille coupling reaction [6] between 4-trimethyl-stannylpyridine and 6-bromo-2,2'-bipyridine as outlined in Scheme 1, we could increase the yield of L to 49%.

The reaction of equimolar amounts of L and AgX (X = BF₄, ClO₄, NO₃, CF₃SO₃) in MeNO₂ resulted in a colourless solution which yielded colourless crystals upon diffusion of diethyl ether into the solution. Nitromethane was used in order to

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SCHEME 1 Reagents and conditions: *i*, toluene/ N_2 , cat. 6% $PdCl_2(PPh_3)_2$ reflux 3 days.

FIGURE 1 The ligand 2,2';6',4''-terpyridine, L, can be thought of as a combination of a chelating 2,2'-bipyridine unit and a terminal pyridine group such that coordination of all three N-donors to a single metal center is impossible.

minimize the involvement of solvent as a ligand which often occurs with better donor solvents such as MeCN, DMF, DMSO or H_2O . In each case, single crystals were analyzed by X-ray diffraction to determine the solid state structure. In no case was $MeNO_2$ involved in coordination to the metal center.

For $X = BF_4$, ClO_4 , and NO_3 , the $[AgL]^+$ cations dimerized to form centrosymmetric $[Ag_2L_2]^{2+}$ clusters as shown in Fig. 2 for $X = BF_4$. The solid state structures are isomorphous for $X = BF_4$ and ClO_4 but the arrangement of dimeric cation and anions is slightly different when $X = NO_3$. The cationic dimers are essentially identical with $Ag...Ag$ distances of 6.570, 6.582 and 6.721 Å for $X = BF_4$, ClO_4 , and NO_3 respectively. The aromatic rings of the pyridine units

are parallel but the distance between the rings is short; ~ 3.2 Å ($N(3)...C(11)'$). So although it may appear as though this aggregate might be a potential host, it is very unlikely that there is room for encapsulation of even the smallest guest. This is supported by the fact that the anion does not occupy this space in any of the structures we studied.

Although the dimers are essentially identical, the way these units are arranged in the solid state is not. The two different arrangements of cation and anion are shown in Fig. 3, A ($X = BF_4$) and B ($X = NO_3$). The two different packing motifs are a direct result of the different ways these anions interact with neighbouring silver atoms. For example, each BF_4 anion sits close to a silver atom ($Ag(1)...F(1)$ 3.24, $Ag(1)...F(2)$ 3.05 Å) but is too distant for further significant interaction with a neighbouring dimer ($Ag(1)'\dots F(3)$ 4.51 Å). The result is a fairly layered structure in which the "neutral" $[Ag_2L_2][BF_4]_2$ units pack with no direct cation-anion interaction between

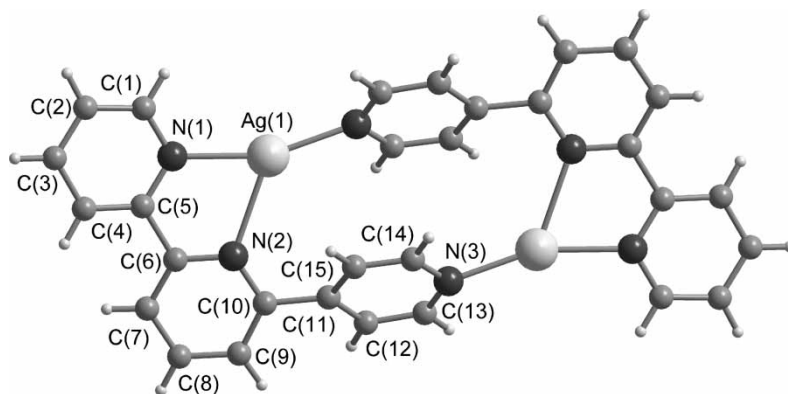


FIGURE 2 X-ray structure of the dimeric cation $[Ag_2L_2]^{2+}$ (anion BF_4) with numbering scheme. Selected distances (Å) and angles ($^\circ$): $Ag(1)-N(1)$ 2.220(6), $Ag(1)-N(2)$ 2.454(5), $Ag(1)-N(3)$ 2.168(5), $Ag(1)-Ag(1')$ 6.570, $N(1)-Ag(1)-N(2)$ 71.3(2), $N(1)-Ag(1)-N(3)$ 160.7(2), $N(2)-Ag(1)-N(3)$ 127.9(2).

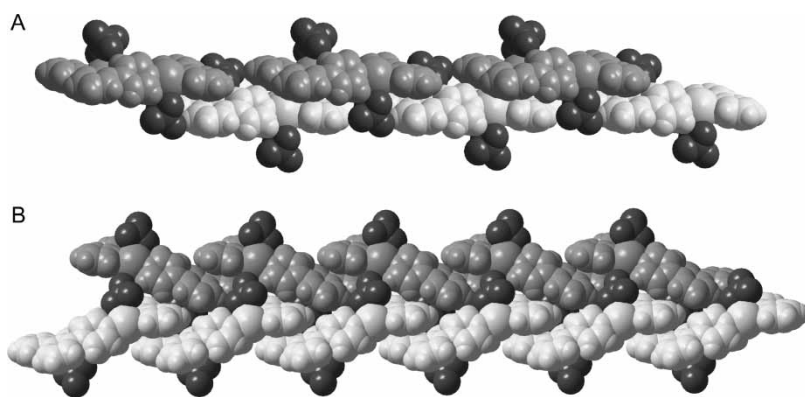


FIGURE 3 X-ray structures of (A) $[\text{Ag}_2\text{L}_2][\text{BF}_4]_2$ and (B) $[\text{Ag}_2\text{L}_2][\text{NO}_3]_2$ showing the packing of cations (alternating gray and light gray) and anions (dark gray). For (A): $\text{Ag}(1)\dots\text{F}(1)$ 3.24, $\text{Ag}(1)\dots\text{F}(2)$ 3.05, $\text{Ag}(1)\dots\text{F}(3)$ 4.51 Å. For (B): $\text{Ag}(1)\dots\text{O}(1)$ 3.19, $\text{Ag}(1)\dots\text{O}(2)$ 2.77, $\text{Ag}(1)\dots\text{O}(3)$ 3.38 Å.

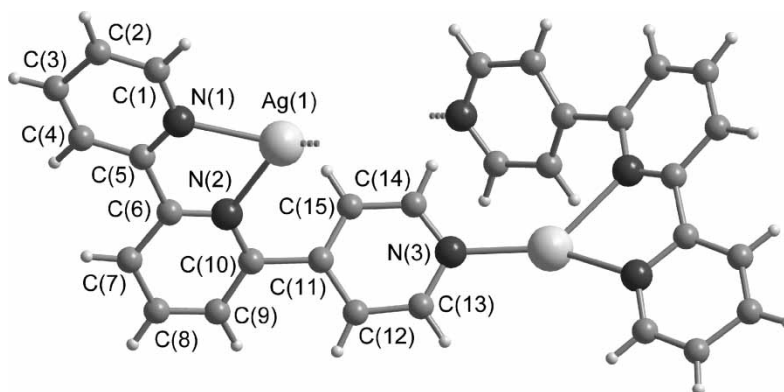


FIGURE 4 Two repeating units of the X-ray structure of the helical polymer cation $[\text{Ag}_2\text{L}_2]^{2+}$ (anion OTf) with numbering scheme. Selected distances (Å) and angles ($^\circ$): $\text{Ag}(1)\text{-N}(1)$ 2.257(4), $\text{Ag}(1)\text{-N}(2)$ 2.403(4), $\text{Ag}(1)\text{-N}(3)$ 2.169(4), $\text{Ag}(1)\dots\text{Ag}(1')$ 6.687, $\text{N}(1)\text{-Ag}(1)\text{-N}(2)$ 71.6(1), $\text{N}(1)\text{-Ag}(1)\text{-N}(3)$ 147.8(1), $\text{N}(2)\text{-Ag}(1)\text{-N}(3)$ 135.4(1).

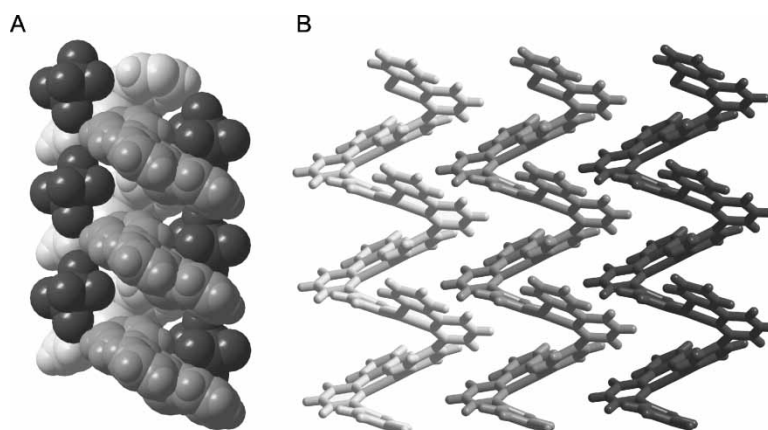


FIGURE 5 X-ray structure of $[\text{Ag}_2\text{L}_2][\text{OTf}]_2$ showing A) a space-filling representation of a single strand of the helical polymer (alternating gray and light gray) with triflate anions (dark gray) and B) a stick representation showing how adjacent helices of the same handedness are arranged.

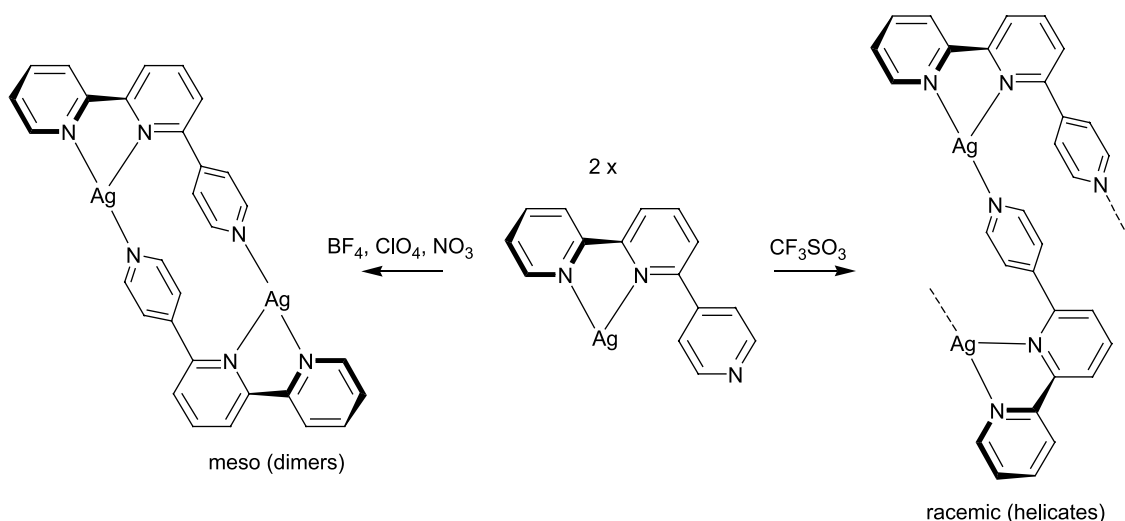


FIGURE 6 Propagation of a pro-chiral monomer results in either a centrosymmetric (dimer) or chiral (helix) aggregate.

them. On the other hand, the NO_3 anions not only interact in a bidentate fashion with one silver atom ($\text{Ag}(1)\dots\text{O}(1)$ 2.78, $\text{Ag}(1)\dots\text{O}(2)$ 3.07) they also undergo a significant secondary interaction with the neighbouring dimer ($\text{Ag}(1')\dots\text{O}(3)$ 3.38 Å). The result is a more angled, herringbone type packing motif that is significantly influenced by the direct intermolecular linking of the dimers through these secondary interactions.

It is interesting to note that the centrosymmetric dimers, $[\text{Ag}_2\text{L}_2]^{2+}$, reported herein are very similar to the complexes $[\text{M}_2\text{L}_2]^{n+}$ ($\text{M} = \text{Ag}(\text{I}), \text{Cu}(\text{II}), \text{Cd}(\text{II})$) reported by Hannon [7,8] for L' , the 4-MeS-derivative of L . However, in none of these cases did the anion interact with the metal centre. Indeed, for Hannon's $[\text{Ag}_2\text{L}'_2]^{2+}$ complex, polymerization was induced by inter-dimer interactions between the external S-donors and neighbouring $\text{Ag}(\text{I})$ ions [7].

The most significant observation to come out of this simple study is that when we change the anion to $\text{X} = \text{CF}_3\text{SO}_3$, the structure no longer consists of closed ring $[\text{AgL}]_2$ dimers but one-dimensional helical $[\text{AgL}]_n$ chains. Figure 4 shows two repeating units of one of these polymer strands.

Figure 5(A) shows the intercalation of CF_3SO_3 anions and AgL cations within an individual helicate strand while Fig. 5(B) shows how individual helicate strands are related in this racemic solid; both hands of the helix are present in the solid state. The pitch of the helix was measured to be 7.37 Å while the diameter of the helical tube of cations and anions is 5.77 Å [9].

The 2,2';6',4''-terpyridine ligand in this study contains three linked aromatic rings all of which can coordinate to a metal centre. The chelating bipyridyl portion has hyper (planar) chirality and coordination to $\text{Ag}(\text{I})$ creates a pro-chiral $[\text{AgL}]^+$ building block. The nature of the counter anion becomes the primary factor in influencing the subtle

balance between the formation of simple *meso* pairs (rings) and the propagation of a topologically distinct curvature into an infinite helix (chains); see Fig. 6.

We conclude that the difference between CF_3SO_3 and BF_4 , ClO_4 , or NO_3 that "controls" the arrangement of $[\text{AgL}]^+$ cations in these structures is basic symmetry. The BF_4 , ClO_4 , and NO_3 anions can interact with metal ions or any Lewis acidic acceptor from any angle (a complete 360° plane or sphere) allowing them to be involved in multiple interactions. However, the CF_3SO_3 ion is more directional with its charge localized on the SO_3 unit and the other end terminated with a neutral CF_3 group. The result is that the BF_4 , ClO_4 , and NO_3 anion structures are more layered because of their ability to undergo some degree of secondary interactions between $\text{Ag}(\text{I})$ ions, while the structure containing the CF_3SO_3 ions is organized into more isolated strands much like a bilayer with the charged SO_3 groups oriented inward and the CF_3 groups on the exterior.

That the observed structure of the cationic portion of the material depends very much on the anion employed is not unique to this system. It is well

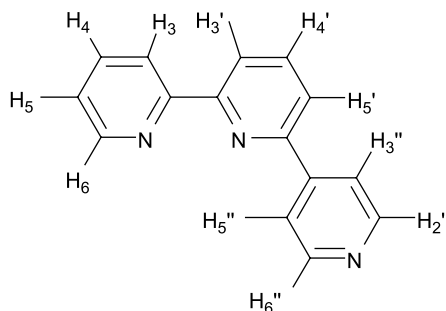


FIGURE 7 The numbering scheme for the ^1H NMR spectrum of 2,2';6',4''-terpyridine, L , above.

TABLE I X-ray crystallographic data collection, solution and refinement parameters for complexes of the type $[\text{AgL}][\text{X}]_n$

Compound	$[\text{AgL}][\text{BF}_4]_2$	$[\text{AgL}][\text{ClO}_4]_2$	$[\text{AgL}][\text{NO}_3]_2$	$[\text{AgL}][\text{OTf}]\cdot\text{MeNO}_2 \cdot n$
CCDC number	266906	266907	266908	266909
Empirical formula	$\text{C}_{30}\text{H}_{22}\text{Ag}_2\text{B}_7\text{F}_8\text{N}_6$	$\text{C}_{30}\text{H}_{22}\text{Ag}_2\text{Cl}_2\text{N}_6\text{O}_8$	$\text{C}_{30}\text{H}_{22}\text{Ag}_2\text{N}_8\text{O}_6$	$\text{C}_{17}\text{H}_{14}\text{AgF}_3\text{N}_4\text{O}_5\text{S}$
Formula weight	887.90	881.18	806.30	551.25
Crystal description	Colourless blocks	Colourless blocks	Colourless blocks	Colourless blocks
Crystal size (mm)	$0.22 \times 0.20 \times 0.16$	$0.24 \times 0.18 \times 0.16$	$0.32 \times 0.26 \times 0.18$	$0.10 \times 0.10 \times 0.10$
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	P-1 (No. 2)	P-1 (No. 2)	P $2_1/n$ (No. 14)	P $2_1/n$ (No. 14)
a (Å)	8.0108 (1)	8.0108 (10)	7.605 (2)	11.0026 (8)
b (Å)	10.3662(2)	10.0603(13)	13.466(3)	7.3776(6)
c (Å)	10.1474 (2)	10.5535 (13)	14.258 (3)	26.0860 (19)
α (°)	74.590 (1)	73.976 (2)	90	90
β (°)	88.644 (1)	69.513 (2)	98.901 (4)	101.198 (2)
γ (°)	69.707 (1)	86.885 (2)	90	90
Z	1	1	2	4
Cell volume (Å ³)	759.75 (2)	771.75 (17)	1442.5 (5)	2077.2 (3)
Density calculated (g cm ⁻³)	1.941	1.896	1.856	1.763
μ (mm ⁻¹)	1.380	1.505	1.418	1.135
Independent reflections (R_{int})	3603 (0.0297)	3333 (0.0155)	5949 (0.0233)	6084 (0.0249)
Data/restraints/parameters	2297/0/218	2191/0/217	2055/0/208	3284/0/281
Goodness-of-fit on F^2	1.146	0.954	1.039	1.096
Final $R1$ [$F^2 > 2\sigma F^2$]	0.0506	0.0285	0.0262	0.0462
Final $wR2$ [$F^2 > 2\sigma F^2$]	0.0598	0.0386	0.0363	0.0581
Final $R1$ (all data)	0.1307	0.0690	0.0584	0.1071
Final $wR2$ (all data)	0.1457	0.0724	0.0620	0.1152
Residuals peak/hole (e/Å ³)	0.758/-0.609	0.441/-0.407	0.508/-0.263	0.422/-0.526

known that the structure of Ag(I) complexes is often dictated by the geometrical requirements of the ligand and the solubility of the resulting salt rather than the coordination chemistry of the metal ion [1–3,10]. However, this is a relatively unique situation for such a simple ligand system. Experiments are currently underway to learn more about this intricate assembly process and control the formation of chiral solid state systems.

EXPERIMENTAL

Synthesis of 2,2':6',4''-terpyridine (L)

A small portion (10% molar) of PdCl₂(PPh₃)₂ (0.149 g, 2.13 × 10⁻¹ mmol) was placed in a Schlenk flask with dry degassed toluene (5 mL) and stirred under N₂ for 30 min. 6Bromo-2,2'-bipyridine [11] (0.550 g, 2.34 mmol) was added under N₂ and stirred for an additional 30 min. To this mixture was added 2 equivalents of 4trimethylstannylpyridine (1.02 g, 4.25 mmol) in toluene (5 mL) via syringe. The mixture was allowed to reflux for 3 days. The reaction was allowed to cool to room temperature and then treated with 2 M HCl (60 mL). The aqueous layer was separated from the toluene layer and basified to pH 9 with NaOH(aq) (5 M). The aqueous layer was extracted with CH₂Cl₂ (3 × 75 mL). The combined organic layers were dried with anhydrous MgSO₄ and the solvent removed by rotary evaporation. The product was purified by sublimation (90°C) and collected as an off-white microcrystalline solid. Yield: 0.245 g (49%). ¹H-NMR (δ, ppm, CDCl₃): 8.72 (dd, ³J_{2''-3''} = ³J_{6'-5''} = 5.3 Hz, ⁴J_{2''-6''} = 1.4 Hz, H_{2''}, H_{6''}), 8.68 (d, ³J₆₋₅ = 9.2 Hz, H₆), 8.56 (d, ³J_{3'-4'} = 7.9 Hz, H_{3'}), 8.45 (d, ³J_{3'-4'} = 7.9 Hz, H₃), 7.98 (dd, ³J_{3''-2''} = ³J_{5''-6''} = 5.3 Hz, ⁴J_{5''-3''} = 1.5 Hz, H_{3''}, H_{5''}), 7.88 (pseudo-t, ³J_{4'-5'} = ³J_{4'-3'} = 7.9 Hz, H_{4'}), 7.83 (td, ³J₄₋₃ = 7.7 Hz, ⁴J₄₋₅ = 1.7 Hz, H₄), 7.78 (d, ³J_{5'-4'} = 7.9 Hz, H_{5'}), and 7.29 (m, H₅) (Fig. 7).

General Synthesis of {[AgL][X]}₂ (X = BF₄, ClO₄, NO₃) and {[AgL][OTf].MeNO₂}}_n

The BF₄ salt is used here as an example but all complexes were prepared in a similar manner. One equivalent of 2,2':6',4''-terpyridine, L, (10.0 mg, 4.29 × 10⁻² mmol) and one equivalent of silver tetrafluoroborate (8.35 mg, 4.29 × 10⁻² mmol) were dissolved in MeNO₂ (2 mL). The mixture was stirred for 5 min. The product precipitated by addition of ⁱPr₂O to yield a white solid. All yields were greater than 95%. The solid was redissolved in MeNO₂ (3 mL) and colourless X-ray quality crystals obtained by slow evaporation of the solution over a period of

72 h. In all cases, over 80% of the product was recovered as crystalline material of a single habit as judged by optical microscopy.

General X-ray Diffraction

All Data were collected on a Brüker SMART CCD instrument at room temperature. Reflection data were integrated from frame data obtained from a hemisphere. Decay (<1%) was monitored by 50 standard data frames measured at the beginning and end of data collection. Diffraction data and unit-cell parameters were consistent with assigned space groups. Lorentzian polarization corrections and empirical absorption corrections, based on redundant data at varying effective azimuthal angles, were applied to the data sets. The structures were solved by direct methods, completed by subsequent Fourier synthesis and refined with full-matrix least squares methods against |F²| data. All non-hydrogen atoms were refined anisotropically. All structural drawings were created using the program DIAMOND [12]. Scattering factors and anomalous dispersion coefficients are contained in the SHELXTL 5.03 program library [13]. A summary of the details of all X-ray data collection, solution and refinement parameters are listed in Table I.

Acknowledgements

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