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Ag(I) Complexes of Imine Derivatives of Unexpected 2-Thiophenemethylamine Homo-Coupling and Bis-(*E*)-*N*-(furan-2-ylmethyl)-1-(quinolin-2-yl)methanimine

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Abstract: Imines are fundamental organic compounds used as synthetic intermediates and as ligands in coordination chemistry. They are also found to be important pharmacophores in various bioactive compounds. In this report, two Schiff bases were prepared using the traditional condensation of 4-pyridinecarboxaldehyde with 2-thiophenemethylamine and 2-quinolinecarboxaldehyde with furfurylamine to form (*E*)-1-(pyridin-4-yl)-*N*-(thiophen-2-ylmethyl)methanimine (**L$_1$**) and (*E*)-*N*-(furan-2-ylmethyl)-1-(quinolin-2-yl)methanimine (**L$_2$**) respectively. **L$_1$** and **L$_2$** were complexed with silver perchlorate in 2:1 [M:L] stoichiometry to obtain complexes **1** and **2**, respectively. The crystal structures of **1** and **2** were unequivocally determined by single-crystal X-ray diffraction analysis. The resulting structures revealed **2** to be a four-coordinate as expected. In contrast, an unexpected chemoselective hydrolytic cleavage of one mole of the (CH=N) imine ligands occurred in complex **2** and, further, the amines (thiophenemethylamine) homo-coupled to form a new imine ligand derivative in situ (**L$_{1a}$**) before coordinating to the Ag(I) center along with **L$_1$**. This observation described an alternative synthetic route to be explored to synthesize a diverse range of imine derivatives, which involves the Ag(I)-promoted homo-coupling of amines. Herein, the crystal structures of Ag(I) complexes of pyridinyl [Ag(**L$_1$**)(**L$_{1a}$**)]ClO$_4$ (**1**) and quinolinyl [Ag(**L$_2$**)$_2$]ClO$_4$ (**2**) Schiff bases are presented.

Keywords: Ag(I) complexes; thiophene; furan; pyridine; quinoline; homo-coupling amines; Schiff bases

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1. Introduction

Schiff bases are one of the most widely used N-donor organic ligands. This can be attributed to their facile synthesis, high stability and high solubility in most organic solvents and their ability to coordinate to various transition metals and a wide range of applications [1,2]. The preparation of Schiff bases can proceed by the condensation reaction of carbonyl compounds with primary amines. Apart from the condensation reaction commonly used in the synthesis of Schiff bases, other synthetic methods have been reported, such as the reductive imination of nitro compounds [3], rebound hydrolysis [4], hydroamination of alkynes with anilines [5], oxidative coupling of alcohols and amines [6] and cross-coupling of amines [7,8].

An organic compound characterized by the presence of a pyridine or quinoline moiety with azomethine linkage to O- or S-heterocycle has been reported to exhibit a broad range of biological activities [9–11]. Their coordination to transition metals has been reported to enhance their biological activities. In this study, crystal structures of Ag(I) perchlorate complexes of pyridinyl (with thiophene moiety) and quinolinyl (with furan moiety) Schiff bases are reported.
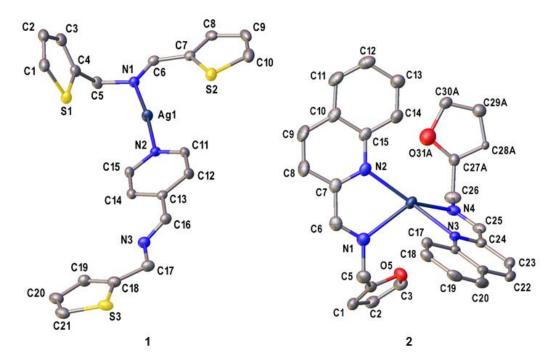
2. Results

The unexpected thiophenemethylamine homo-coupling pyridinyl imine Ag(I) complexes (1) and quinolinyl imine Ag(I) complexes (2) were prepared by reaction of either L_1 or L_2 with silver perchlorate in 2:1 (L:M) stoichiometry. The four-coordinate complex **2** was isolated as proposed but in an attempt to complex **L_1** ((*E*)-1-(pyridin-4-yl)-*N*-(thiophen-2-ylmethyl)methanimine) with silver perchlorate in 2:1 (L_1:M), a chemoselective hydrolytic cleavage of the (-CH=N) imine bond of one of the two ligands occurred. This is followed by instant cross-coupling of the thiophene amines in the presence of a Ag(I) ion to form a new imine ligand ((*E*)-1-(thiophen-2-yl)-*N*-(thiophen-2-ylmethyl)methanimine L_{1a}). Afterward, L_1 and L_{1a} coordinated to the Ag(I) ion leading to a linear Ag(I) complex (1). This method of imine synthesis agrees with that from the literature [8], where transition metals act as a catalyst during the formation of imine from amines. The possibility of imine metathesis could be inconsequential since after the chemoselective hydrolytic cleavage of one molecule of the (CH=N) imine ligands, there seem to be no exchange equilibria of the R groups between the two molecules of the Schiff bases. The structures of **1** and **2** were confirmed by NMR, FT-IR, UV-vis, Mass spec, elemental analysis and X-ray diffraction.

The ^{1}H NMR spectrum of **1** exhibits two singlets assigned to imine (CH=N) protons at 8.63 and 8.54 ppm signifying their different resonance. The signal of the -CH$_2$ protons for the two ligands was seen as singlets at 4.91 and 5.01 ppm. The integration values and the significant downfield shifts in the newly formed (L_{1a}) imine proton, the CH$_2$ protons and the alpha proton on the pyridine ring relative to L_1 resonance peaks (Figure S5) confirmed the confirmed the mode of coordination in complex 1 to be via the pyridinyl (N_{py}) and the imine nitrogen (N_{im}) atoms. In the ^{1}H NMR spectrum of **2,** the azomethine alpha protons and the alpha proton on the quinoline ring shifted downfield relative to the free L_2 resonance peaks (Figure S4). This confirmed the coordination of complex 2 to be via the N_{im} and N_{qy} atoms in an *N,N*-bidentate manner. The coordination mode in complex 2 is similar to the reported four coordinate Ag(I) complexes [12]. Electronic absorption spectra of the complexes were recorded in acetonitrile at room temperature in the UV-Vis region. The absorption spectra of 1 (Figure S1) showed two absorption bands at 292 nm and 365 nm and red-shifted with respect to L_1 absorption bands. These absorption bands are attributable to π–π* and n–π* transitions of the imine and pyridine ring. In **2**, only one absorption band (Figure S2) at 313 nm assigned to π–π* transition was seen. Complex 2 red-shifted with respect to its free ligand L_2, similar to reported quinolinyl Ag(I) complexes [13]. In the FT-IR spectroscopy study of 1 and 2 (Figures S13 and S14), a sharp absorption band assigned to imines at 1609 cm^{-1} and 1620 cm^{-1} respectively, were observed. These imine absorption bands shifted to lower frequencies with respect to their free ligands suggesting the coordination of the free ligands to Ag(I) ion. The calculated molecular formula of 1 [C$_{21}$H$_{19}$AgN$_3$S$_3$]$^+$ and 2 [C$_{30}$H$_{24}$AgN$_4$O$_2$]$^+$ agreed with their found molecular ion peak at m/z 518 and m/z 581 respectively obtained in the positive ion mode. The microanalyses of **1** and **2** are in good accordance with the reported structures.

Crystal Structures

Crystals of **1** and **2** suitable for X-ray crystallography were obtained by diffusing hexane into dichloromethane solutions of **1** to obtain a yellow block of **1**, while for **2**, slow diffusion of toluene into dichloromethane solutions of **2** was done to obtain a brown needle crystal. The asymmetric unit of **1** and **2** consist of a cationic complex bearing one Ag(I) center and two imine ligand derivatives with one perchlorate counterion and a hydrate molecule as shown in Figure 1. Complex **1** has a mixed ligand system which comprises of **L_1** and **L_{1a}**. Furthermore, L_1 and L_{1a} coordinate to the Ag(I) center via the pyridinyl (N_{py}) and the imine nitrogen (N_{im}) atoms, respectively. This results in a distorted linear geometry [14] around the metal center with an N_{py}—Ag—N_{im} bond angle of 174.31(8)°. Interestingly, intramolecular Ag1 . . . S1 (3.2622(9) Å, symmetry code: *x, y, z*) and intermolecular Ag1 . . . S3 (3.169(1) Å, symmetry code: 1-*x*, 2-*y*,2-*z*) interactions were found to be shorter than the sum of the van der Waals radii (3.52 Å) [15,16]. Unlike in 1, the Ag(I) center in

2 is coordinated to two identical (*E*)-*N*-(furan-2-ylmethyl)-1-(quinolin-2-yl)methanimine ligands which exhibit a $\kappa^2 N,N'$ coordination mode. The coordination environment around the metal center is occupied by two quinolinyl nitrogen (N_{qy}) and N_{im} atoms from separate ligands. Moreover, the τ_4 value of complex **2** is equal to 0.83, indicating its distorted trigonal pyramidal geometry [17] with N—Ag—N bond angles ranging between 99.46(7)° and 143.77(8)°. Other selected bond parameters in **1** and **2** are listed in Table 1 and are comparable with those of closely related compounds in the literature [18,19].

Figure 1. The ORTEP diagrams of complexes **1** and **2** with the thermal ellipsoids drawn at the 50% probability level. The hydrate molecule in **1** including all hydrogen atoms and perchlorate anions in both complexes have been omitted for clarity.

Table 1. Selected geometric parameters for complexes **1** and **2**.

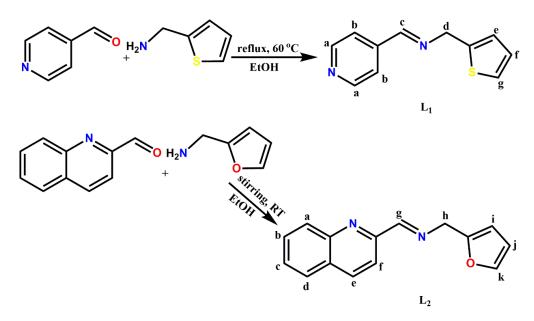|	1	2
Ag—N_{py}	2.123(2)	
Ag—N_{qy}		2.272(2)
		2.377(2)
Ag—N_{im}	2.122(2)	2.377(3)
		2.265(2)
N_{py}—Ag—N_{im}	174.31(8)	
		143.77(8)
N_{qy}—Ag—N_{im}		99.46(7)
		72.06(7)
		72.01(7)

3. Materials and Methods

Ethanol 99.5% (Aldrich, St. Louis, Missouri, MO, USA), diethyl ether 99.8% (Aldrich, St. Louis, Missouri, MO, USA), DMSO-d_6 99.8% (Merck, Darmstadt, Germany), 4-pyridinecarboxaldehyde 99% (Aldrich, St. Louis, Missouri, MO, USA), 2-quinolinecarboxaldehyde 99% (Aldrich, St. Louis, Missouri, MO, USA), 2-thiophenemethylamine > 92% (MerckDarmstadt, Germany), furan-2-ylmethanamine 99% (Aldrich, St. Louis, Missouri, MO, USA), dichloromethane 99% (Aldrich, St. Louis, Missouri, MO, USA), and nitrogen gas, 5.0 technical grade (Air flex Industrial Gases, Pietermaritzburg, Africa) were purchased

from local suppliers. All chemicals were analytical grade and were used as received, while most of the solvents were dried using conventional techniques.

^{1}H NMR and ^{13}C NMR spectra were recorded on a BRUKER 400 MHz spectrometer in DMSO-d_6 and acetone-d_6. Chemical shift values are reported in parts per million (ppm) relative to the solvent residual peaks in DMSO-d_6 and acetone-d_6; 2.5 and 2.05 ppm respectively for ^{1}H NMR and 39.5 and 29.4 ppm respectively for ^{13}C NMR. The splitting patterns in ^{1}H NMR spectra are reported as s for singlet, d for doublet, m for multiplet and J (the coupling constant is given in Hertz). The infrared spectra were recorded using a PerkinElmer Spectrum 100 FT-IR spectrometer, and the data are reported as percentage transmittances at the respective wavenumbers (cm^{-1}), between 4000 and 650 cm^{-1}. The mass spectra were recorded using the Shimadzu LCMS-2020 instrument with only molecular ions (M$^+$) and major fragmentation peaks being reported with intensities quoted as percentages of the base peak. Elemental analyses were performed on Thermal-Scientific Flash 2000 CHNS/O analyzer. All melting points were determined using the Stuart Scientific melting point apparatus.

3.1. Synthesis of Pyridinyl (L$_1$) and Quinolinyl (L$_2$) Schiff bases

Ligands (*E*)-1-(pyridin-4-yl)-*N*-(thiophen-2-ylmethyl)methanimine (**L$_1$**) and (*E*)-*N*-(furan-2-ylmethyl)-1-(quinolin-2-yl)methanimine (**L$_2$**) (Scheme 1) were prepared using similar methods reported by our group [20,21].

Scheme 1. Synthesis of pyridinyl (**L$_1$**) and quinolinyl (**L$_2$**) Schiff bases.

Synthesis of **L$_1$**: 4-pyridinecarboxaldehyde (1 mmol, 0.11 g, 0.09 mL) in anhydrous ethanol (10 mL) was added slowly to a stirred hot solution of 2-thiophenemethylamine (1 mmol, 0.11 g, 0.10 mL) in anhydrous ethanol (10 mL) in the presence of a few drops of glacial acetic acid. The reacting mixture was reflux at 80 °C for 4 h. The resulting reaction solution was dried over anhydrous MgSO$_4$, filtered and concentrated under reduced pressure. The yellow oil obtained was recrystallized from ethanol. Yield: 0.18 g, 89%, ^{1}H-NMR (400 MHz, (CD$_3$)$_2$CO, δ ppm): 8.69 (2H, m, Hb-C$_5$H$_4$N), 8.48 (1H, s, Hc-CH=N-), 7.71 (2H, m, Ha-C$_5$H$_4$N), 7.36 (1H, s, Hg-C$_4$H$_4$S), 7.03 (1H, m, He-C$_4$H$_4$S), 7.00 (1H, m, Hf-C$_4$H$_4$S), 5.03 (2H, s, Hd-CH$_2$). ^{13}C-NMR (100 MHz, (CD$_3$)$_2$CO, 25 °C): δ = 156.24 (C6-C=N-), 151.04 (C5-C$_5$H$_4$N), 150.02 (C2 & C3-C$_5$H$_4$N), 140.56 (C8- C$_4$H$_3$S), 127.22 (C10-C$_4$H$_3$S), 125.17 (C9- C$_4$H$_3$S), 124.87 (C11-C$_4$H$_3$S), 121.66 (C1 & C4-C$_5$H$_4$N), 58.96 (C7-CH$_2$). FT-IR (cm^{-1}): (-C=N-) 1628, (pyridinyl) 1596, (CH$_2$) 1411, (thiophene) 698. UV/Vis (CH$_3$CN): λ_{max} 287, 363 nm. MS: *m/z* Calcd. For [C$_{11}$H$_{10}$N$_2$S]: 202.28; found [3L$_1$ + 3MeOH]$^+$: 705 (100%), [L$_1$]$^+$ 203 (69%), [L$_1$ + MeOH]$^+$ 33%.

Synthesis of **L₂**: Ligand **2** was synthesized by the gradual addition of 2-quinoline-carboxaldehyde (1 mmol, 0.16 g) dissolved in anhydrous ethanol (10 mL) to a solution of furfurylamine (1 mmol, 0.10g, 0.09 mL), respectively, in anhydrous ethanol (10 mL) in the presence of glacial acetic acid. The reactant mixture was subjected to constant stirring at ambient temperature for 6 h. Afterward, the resulting solution was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to obtain a yellow oil product. The oil obtained was recrystallized from ethanol. Yield: 0.21 g, 88%, ^{1}H-NMR (400 MHz, $(CD_3)_2CO$, δ ppm): 8.57 (1H, d, J = 0.82 Hz, Hg-CH=N-), 8.37 (1H, d, J = 8.63 Hz, Hd-C_9H_6N), 8.16 (1H, d, J = 8.55 Hz, Hd-C_9H_6N), 8.09 (1H, d, J = 9.56 Hz, Ha-C_9H_6N), 7.99 (1H, m, Hf-C_9H_6N), 7.80 (1H, m, Hb-C_9H_6N), 7.65 (1H, m, Hc-C_9H_6N), 7.53 (1H, m, Hk-C_4H_3O), 6.41 (2H, m, Hj, i-C_4H_3O), 4.90 (2H, d, J = 1.31 Hz, Hh-CH_2). ^{13}C-NMR (100 MHz, $(CD_3)_2CO$, 25 °C): δ = 153.70 (C9-C_9H_6N), 152.17 (C10-C=N-), 149.20 (C12-C_4H_3O), 147.86 (C1-C_9H_6N), 142.26 (C15-C_4H_3O), 137.63 (C7-C_9H_6N), 130.92 (C6-C_9H_6N), 130.51 (C3-C_9H_6N), 129.66 (C2-C_9H_6N), 128.69 (C5-C_9H_6N), 128.22 (C4-C_9H_6N), 121.62 (C8-C_9H_6N), 110.97 (C14-C_4H_3O), 108.15 (C13-C_4H_3O), 48.88 (C11-CH_2). FT-IR (cm^{-1}): (Ar-CH) 3055, (-C=N-) 1641, (quinolinyl) 1594, (CH_2) 1425, (furan), 734. UV/Vis (CH_3CN): λ_{max} 295 nm. MS: m/z Calcd. For $[C_{15}H_{12}N_2S]$: 252.34; found $[2L_2 + CH_3CN]^+$: 547 (100%), $[2L_2 + Na + 2H)]^+$ 531 (36%), $[L_2 + 2CH_3CN + Na + 2H]$ 360 (25%).
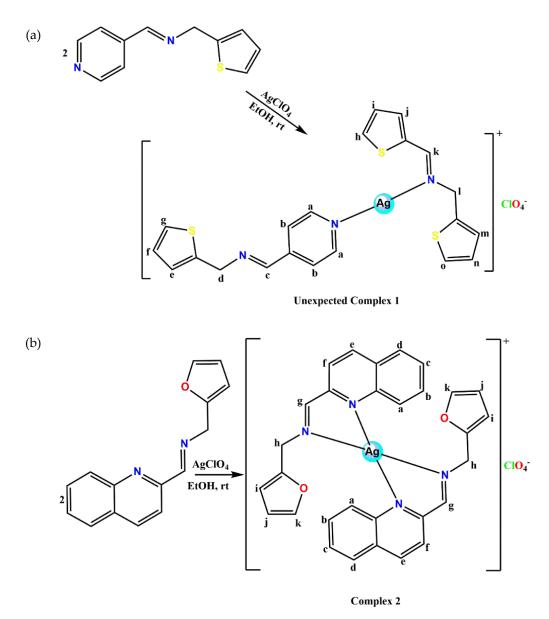
3.2. Synthesis of Pyridinyl and Quinolinyl Ag(I) Complexes

A slightly modified procedure from our group was also used [22,23] in the synthesis of the Ag(I) complexes as shown in Scheme 2a,b.

Complex 1: **L₁** (5 mmol, 1.01 g) dissolved in anhydrous ethanol (15 mL) was added dropwise to an ethanolic (15 mL) solution of silver perchlorate (2.5 mmol, 0.52 g) under constant stirring in the dark. The reaction was carried out under nitrogen at ambient temperature for 6 h. The resulting solid precipitate was isolated using a vacuum filter. Afterwards, the precipitate was washed with cold ethanol (10 mL X2) followed by cold ether (10 mL X2) and dried in *vacuo.* The yellow precipitate isolated was recrystallized by diffusing hexane into dichloromethane solutions of the complexes to obtain a yellow block crystal suitable for X-ray crystallography. Yield: 0.79 g, 52%, M.pt. 161–162 °C. ^{1}H-NMR (400 MHz, DMSO-d_6, δ ppm): 8.69 (2H, m, Hb-C_5H_4N), 8.63 (1H, s, Hc-C=N), 8.54 (1H, s, Hl-C=N), 7.75 (2H, m, Ha-C_5H_4N), 7.55 (1H, m, Hm-C_4H_3S), 7.43 (3H, m, Hg, h, o-C_4H_3S), 7.27 (3H, m, Hf, i, n-C_4H_3S), 7.02 (2H, m, He, j-C_4H_3S), 5.01 (2H, s, Hd-CH_2), 4.91 (2H, s, Hk-CH_2). ^{13}C-NMR (100 MHz, DMSO-d_6, 25 °C): δ = 160.89 (C16-C=N-), 156.47 (C6-C=N-), 150.70 (C7-C_5H_4N), 150.12 (C10-C_5H_4N), 150.08 (C11-C_5H_4N), 139.05 (C4-C_4H_3S), 138.49 (C18-C_4H_3S), 127.97 (C14-C_4H_3S), 127.58 (C13-C_4H_3S), 127.02 (C20-C_4H_3S), 126.99 (C2-C_4H_3S), 126.50 (C3 & 19-C_4H_3S), 125.99 (C12-C_4H_3S), 125.35 (C1 & C21-C_4H_3S), 125.33 (C15-C_4H_3S), 125.29 (C8 & C9-C_5H_4N), 58.40 (C5-CH_2), 57.89 (C17-CH_2). FT-IR (cm^{-1}): (pyridinyl) 1609, (-C=N) 1609, (CH_2) 1424, (thiophene) 706. UV/Vis (CH_3CN): λ_{max} 292, 365 nm. MS: m/z Calcd. For $[C_{21}H_{19}AgN_3S_3]$: 517.45; found $[Ag(L_1)_2 + 3CH_3CN]^+$: 641 (100%). Anal. Calcd. (%) for $[C_{21}H_{19}AgClN_3O_4S_3]$: C, 40.89; H, 3.10; N, 6.81; found (%): C, 40.72; H, 3.06; N, 6.75.

Complex 2: **L₂** (2 mmol, 0.51 g) dissolved in anhydrous ethanol (10 mL) was added dropwise to an ethanolic (10 mL) solution of silver perchlorate (1 mmol, 0.21 g) under constant stirring in the dark. The reaction was carried out under nitrogen at ambient temperature for 6 h. A brown solid product was obtained and isolated using a vacuum filter. Afterwards, the brown solid product was washed with cold ethanol twice followed by cold ether (10 mL X2) and dried in *vacuo.* The brown solid was recrystallized by diffusing toluene into dichloromethane solutions of the complexes to obtain a brown needle crystal suitable for X-ray crystallography. Yield: 0.63 g, 93%, Melting point: 149–151 °C, ^{1}H-NMR (400 MHz, $(CD_3)_2CO$, δ ppm): 8.90 (2H, s, Hg-CH=N-), 8.70 (2H, d, J = 8.44 Hz, He-C_9H_6N), 8.11 (4H, m, Hd, a-C_9H_6N), 8.03 (2H, d, J = 8.63 Hz, Hf-C_9H_6N), 7.87 (2H, t, Hb-C_9H_6N), 7.74 (2H, t, Hc-C_9H_6N), 7.56 (2H, d, J = 1.13 Hz, Hk-C_4H_3O), 6.51 (2H, m, Hj-C_4H_3O), 6.45 (1H, m, Hi-C_4H_3O), 6.39 (1H, t, J = 2.47 Hz, Hi-C_4H_3O), 5.01 (2H, s, m, Hh-CH_2), 4.08

(2H, s, Hh-CH$_2$). ^{13}C-NMR (100 MHz, (CD$_3$)$_2$CO, 25 °C): δ = 163.47 (C10-C=N-), 150.93 (C9-C$_9$H$_6$N), 149.98 (C12-C$_4$H$_3$O), 145.91 (C1-C$_9$H$_6$N), 143.09 (C15-C$_4$H$_3$O), 139.46 (C7-C$_9$H$_6$N-), 131.67 (C6-C$_9$H$_6$N), 129.80 (C3-C$_9$H$_6$N), 129.31 (C2-C$_9$H$_6$N), 128.75 (C5-C$_9$H$_6$N), 128.34 (C4-C$_9$H$_6$N), 123.36 (C8-C$_9$H$_6$N), 110.63 (C14-C$_4$H$_3$O), 108.78 (C13-C$_4$H$_3$O), 55.82 (C11-CH$_2$). FT-IR (cm^{-1}): (-C=N-) 1620, (quinolinyl) 1586, (CH$_2$) 1433, (furan) 752. UV/Vis (CH$_3$CN): $\lambda_{\max}$ 313 nm. MS: *m/z* Calcd. for [C$_{30}$H$_{24}$AgN$_4$O$_2$]: 580.42; found [Ag(L$_2$)$_2$ + 2CH$_3$CN + K]$^+$: 705 (100%). Anal. Calcd. (%) for [C$_{30}$H$_{24}$AgClN$_4$O$_6$]: C, 53.00; H, 3.56; N, 8.24; found (%): C, 53.11; H, 3.32; N, 8.02.

Scheme 2. (**a**) Synthesis of Ag(I) complex of imine derivatives (**1**); (**b**) Synthesis of Ag(I) complex of quinolinyl Schiff bases (**2**).

3.3. X-ray Crystallography

Crystal evaluation and data collection of the complexes **1** and **2** were recorded on a Bruker Apex Duo diffractometer equipped with an Oxford Instruments Cryojet operating at 100 (2) K and an Incoatec microsource operating at 30 W power. The data were collected with Mo Kα (λ = 0.71073 Å) radiation at a crystal-to-detector distance of 50 mm using omega and phi scans. The data were reduced with the program SAINT [24] using outlier rejection, scan speed scaling, as well as standard Lorentz and polarization correction

factors. A SADABS [25] semi-empirical multi-scan absorption correction was applied to the data. The structures of complexes **1** and **2** were solved by the direct method using the SHELXS [26] program and refined. The visual crystal structure information was performed using ORTEP-3 [27], system software. Non-hydrogen atoms were first refined isotropically and then by anisotropic refinement with a full-matrix least-squares method based on F^2 using SHELXL [28]. All hydrogen atoms were positioned geometrically, allowed to ride on their parent atoms, and refined isotropically. The crystallographic data and structure refinement parameters of complexes **1** and **2** are given in Table 2. The two thiophenyl rings in **1** were found to be disordered over two positions. PART instructions were used to resolve the disorder, with the major components having 0.6 and 0.9 site occupancy factors. In **2**, the furanyl ring and the perchlorate anion exhibited disorder over two positions. PART instructions were used to model the disorder and the major component had 0.722(8) site occupancy factor.

Table 2. Crystal data and structure refinement for complexes **1** and **2**.

	1	**2**
Chemical formula	$C_{21}H_{19.9}AgClN_3O_{4.13}S_3$	$C_{30}H_{25}AgClN_4O_{6.25}$
Formula Weight	619.80	684.86
Crystal system	Triclinic	monoclinic
Space group	P-1	C2/c
a(Å)	10.8978(5)	21.4229(10)
b(Å)	11.0223(5)	15.9905(10)
c(Å)	11.7827(5)	18.1880(9)
$\alpha(°)$	97.086(2)	90
$\beta(°)$	116.347(4)	116.615(3)
$\gamma(°)$	107.320(3)	90
$V(Å^3)$	1155.54(10)	5570.3(5)
Z	2	8
$\rho_{calc}(gcm^{-3})$	1.781	1.633
μ (mm^{-1})	1.295	0.873
F(000)	624.0	2776.0
Crystal size (mm^3)	$0.2 \times 0.18 \times 0.14$	$0.26 \times 0.12 \times 0.08$
θ range for data collection (°)	4.042 to 55.75	3.318 to 56.514
Index ranges	$-14 \leq h \leq 14,$ $-14 \leq k \leq 8,$ $-15 \leq l \leq 15$	$-28 \leq h \leq 28,$ $-21 \leq k \leq 21,$ $-24 \leq l \leq 24$
Reflections collected	20931	49838
Independent reflections	5488 [R$_{int}$ = 0.0195, R$_{sigma}$ = 0.0200]	6881 [R$_{int}$ = 0.0297, R$_{sigma}$ = 0.0176]
Completeness to theta = 28.96	99.5%	100.0%
Data / restraints / parameters	5488/198/379	6881/139/469
Goodness-of-fit on F^2	1.050	1.053
R indices [I > 2sigma(I)]	R$_1$ = 0.0274, wR$_2$ = 0.0668	R$_1$ = 0.0323, wR$_2$ = 0.0844
R indices (all data)	R$_1$ = 0.0303, wR$_2$ = 0.0685	R$_1$ = 0.0367, wR$_2$ = 0.0876
Largest diff. peak and hole (e Å^{-3})	1.06 and -0.60	1.19 and -0.77

4. Conclusions

The conversion of amines to imines in the presence of Ag(I) ion as a catalyst, without being under aerobic conditions or any other additives, has been demonstrated herein. The homo-coupling of thiophene amines derived from the selective hydrolytic cleavage of an imine bond to form a new imine yielded a linear Ag(I) complex of imine derivatives (1). In complex 2, the quinolinyl Schiff base adopts a pseudo-trigonal pyramidal geometry around the Ag(I) center. The spectroscopic data confirmed the structures of complexes 1 and 2.

The comparison of the crystal structures of **1** and **2** revealed their different structural features. Interestingly, both complexes were prepared from silver perchlorate complexes of either pyridinyl (**L₁**) or quinolinyl (**L₂**) Schiff bases, with each ligand having a methylene linker to a five-member heterocyclic moiety. However, the conjugated ring and the position

of the N atom in **2** must have influenced its stability in the presence of the Ag(I) ion. As such, **L₂** coordinated as expected in an *N,N*-bidentate manner (**2**). Considering the cost-effectiveness of anilines and the availability of silver salts, this report has proven a facile reaction route at ambient temperature and mild reaction conditions to explore the synthesis of a diverse range of silver-promoted imine derivatives.

Supplementary Materials: The following are available online. Figures S1 and S2: Electronic absorption spectra of **L₁**, **L₂**, complexes **1** and **2**, Figures S3–S6: ^{1}H NMR spectra of **L₁** and **L₂** and **1** and **2**, Figures S3–S6: ^{13}C NMR spectra of **L₁** and **L₂** and **1** and **2**, Figures S7–S10: IR spectra of **L₁** and **L₂** and **1** and **2**, Figure S11–S14: Mass Spec. spectra of **L₁** and **L₂** and **1** and **2**: Figures S15–S18.

Author Contributions: B.O. conceived and designed the experiments; A.A.A. carried out the synthesis, crystal growth and characterized the reported structures. A.A.A. drafted the manuscript; S.J.Z. reported the crystal structures; B.O. revised the manuscript. All authors have read and agreed to the published version of the manuscript.

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