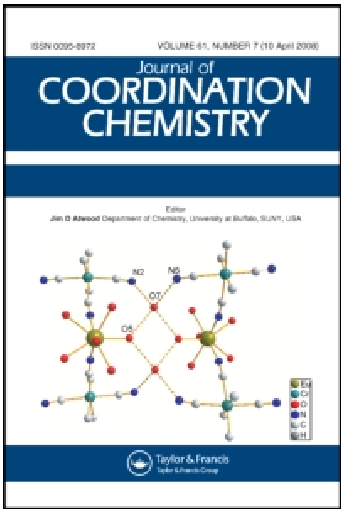

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Syntheses and supramolecular structures of silver(I) complexes based on 2-(2'-pyridyl)-quinoxaline

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Syntheses and supramolecular structures of silver(I) complexes based on 2-(2′-pyridyl)-quinoxaline

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Three mononuclear complexes [$AgL_2 \cdot X$] (**L** = 2-(2′-pyridyl)-quinoxaline, X = ClO_4^-, **1**, PF_6^-, **2**, and $CF_3SO_3^-$, **3**) and one 1-D organic–inorganic coordination polymer $[Ag_2L(CF_3CO_2)_2]_n$ (**4**) were obtained. Anions of ClO_4^-, PF_6^-, and $CF_3SO_3^-$ are non-coordinated counter-ions of $(AgL_2)^+$ cations with bidentate-chelated **L** (Mode I in scheme 1), while two bridging $CF_3CO_2^-$ anions connect adjacent $(Ag_2L)^{2+}$ cations with mixed bidentate–monodentate **L** (Mode II in scheme 1), leading to formation of a 1-D infinite linear chain network. Complicated supramolecular interactions involving the anions in all four complexes result in multidimensional networks.

Keywords: 2-(2′-Pyridyl)-quinoxaline; Ag(I) coordination complexes; Anion controlling; Supramolecular interactions

1. Introduction

Labile Ag(I) complexes are of current interest for potential as functional materials [1] and novel networks [2]. Ag(I) has varied coordination geometries from linear [3], trigonal [4], tetrahedral [5], square planar [6], square pyramidal [7], trigonal prism [8] to octahedral [9]. Diverse supramolecular interactions, such as hydrogen bonding ($C–H \cdots X$, X = donor atom, or $C–H \cdots \pi$), Ag–Ag interaction, and π–π stacking, are incorporated with the Ag-ligand coordination interaction, selection of functional ligands [10], control of anions [11], and solvent effects [12]. In contrast to the well-developed cationic coordination chemistry [13], coordination chemistry of anions has received less attention due to the less effective electrostatic interactions [14]. Growth of this area results from its interest in biological systems, medicine, catalysis, and environmental issues [15]. In spite of the recent advances in anionic supramolecular chemistry, the characteristic features of anions, such as lower charge to radius ratio

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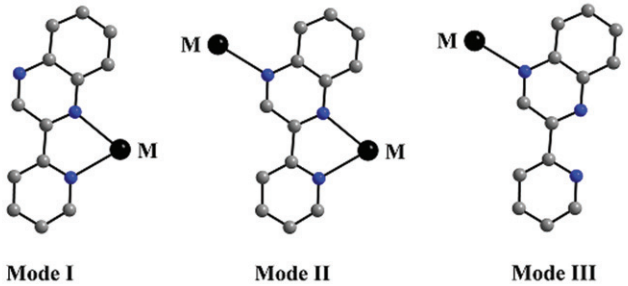

Scheme 1. Schematic view of the coordination mode of *L*: Mode I, bidentate; Mode II, mixed bidentate–monodentate; Mode III, monodentate.

than isoelectronic cations, structural variety or sensitivity to pH, provide challenges to control of molecular frameworks.

2-(2′-Pyridyl)-quinoxaline (**L**, as shown in scheme 1) [16], first reported from the unexpected reaction between 2-acetyl-pyridine and 1,2-phenylenediamine, is a promising candidate for combining the chelating ability of 2,2′-bipyridine with the bridging of quinoxaline. Complexes of such ligand could be used to model bioinorganic systems and have potential applications as photo-sensitizers, catalysts, and electronic conductors [17]. Mononuclear or binuclear Cu^+ [18] or M^{2+} (M = Cu [19], Co [20], Ni [20], Mn [21], Pd [22], Hg [23], or Ir [24]) complexes from bidentate chelated (Mode I in scheme 1) **L** were obtained, while surprisingly little effort has been directed towards the study of its Ag^+ complexes [25]. The mixed bidentate–monodentate mode (Mode II in scheme 1) of **L** has not been observed. Herein, we describe the roles of anions on the self-assembly of a series of AgX ($X = ClO_4^-$, PF_6^-, $CF_3SO_3^-$, and $CF_3CO_2^-$) with **L**, showing that changing the counter-ion of Ag^+ significantly changed the structures, and various supramolecular interactions led to different multidimensional networks.

2. Experimental

2.1. *Materials and methods*

All chemicals were commercially available of reagent grade and used without purification. Infrared spectra were recorded on a Bruker EQUINOX55 FT-IR spectrophotometer in the region 4000–400 cm^{-1} in KBr pellets. Elemental analyses were performed on a Perkin-Elmer Model 240C elemental analyzer.

2.2. *Syntheses*

Caution! Perchlorate salts are potentially explosive. Only a small amount of materials should be prepared and should be handled with care.

2.2.1. Preparation of $Ag(L)_2 \cdot ClO_4$ (1). A solution of 0.05 mmol of $AgClO_4$ (11 mg) in 3 mL of CH_3CN was added dropwise to a stirred solution of 0.05 mmol of **L** (16 mg) in

3 mL of CH_3CN at room temperature. The yellow clear solution was stirred for another 0.5 h and filtered; Et_2O was diffused into the filtrate slowly over 3 weeks at room temperature to give yellow block crystals. Yield: 65%. Increase of the metal-to-ligand ratio (2 : 1) leads to formation of the same product of better crystal quality with somewhat high yield (67%). Anal. Calcd for $C_{26}H_{18}AgClN_6O_4$ (%): C, 50.22; H, 2.92; N, 13.52. Found: C, 50.11; H, 3.01; N, 13.39. IR(KBr, cm^{-1}): 3450 (w), 3052 (w), 1592 (w), 1545 (w), 1500 (w), 1475 (m), 1208 (m), 1164 (w), 1116 (s), 1070 (m), 1046 (w), 1003 (w), 966 (s), 777 (s), 741 (m), 712 (w), 549 (w), 453 (w).

2.2.2. Preparation of $Ag(L)_2 \cdot PF_6$ (2). The reaction was carried out in the same way as for **1** except that $AgPF_6$ (13.0 mg, 0.05 mmol) was used instead of $AgClO_4$. Yellow prism crystals of **2** were obtained after two weeks at room temperature. Yield: 59%. Anal. Calcd for $C_{26}H_{18}AgF_6N_6P$ (%): C, 46.70; H, 2.72; N, 12.59. Found: C, 46.61; H, 2.81; N, 12.42. IR(KBr, cm^{-1}): 3442 (w), 1647 (w), 1596 (w), 1546 (w), 1472 (m), 1420 (w), 1322 (w), 1209 (m), 1112 (w), 1052 (w), 1009 (m), 964 (s), 837 (vs), 776 (s), 730 (m), 664 (w), 552 (s).

2.2.3. Preparation of $Ag(L)_2 \cdot CF_3SO_3$ (3). The reaction was carried out in the same way as for **1** except that $AgCF_3SO_3$ (13.0 mg, 0.05 mmol) was used instead of $AgClO_4$. Yellow block crystals of **3** were obtained after one week at room temperature. Yield: 63%. Anal. Calcd for $C_{27}H_{18}AgF_3N_6O_3S$ (%): C, 48.30; H, 2.70; N, 12.52. Found: C, 48.48; H, 2.75; N, 12.45. IR (KBr, cm^{-1}): 3449 (w), 1645 (w), 1595 (w), 1546 (w), 1472 (m), 1428 (w), 1369 (w), 1262 (vs), 1134 (s), 1032 (s), 965 (s), 780 (m), 735 (m), 635 (s), 549 (w), 512 (w).

2.2.4. Preparation of $[Ag_2L(CF_3CO_2)_2]_n$ (4). The reaction was carried out in the same way as for **1** except that $AgCF_3CO_2$ (11.0 mg, 0.05 mmol) was used instead of $AgClO_4$. Yellow prism crystals of **4** were obtained after 10 days at room temperature. Yield: 63%. Anal. Calcd for $C_{17}H_9Ag_2F_6N_3O_4$ (%): C, 31.46; H, 1.40; N, 6.47. Found: C, 31.38; H, 1.45; N, 6.35. IR (KBr, cm^{-1}): 3345 (w), 3052 (w), 1685 (vs), 1593 (m), 1546 (w), 1538 (s), 1473 (m), 1427 (m), 1371 (m), 1322 (w), 1192 (s), 1110 (vs), 1004 (w), 957 (s), 788 (s), 740 (w), 711 (w), 666 (w), 635 (w), 549 (w), 497 (w).

2.3. *X-ray crystallography*

Single crystals of **1**–**4** were mounted onto thin glass fibers. All intensity data were collected on a Bruker SMART CCD diffractometer (Mo-Kα radiation, $\lambda = 0.71073$ Å) in ϕ and ω scan modes at room temperature (293(2) K). Structures of the four complexes were solved by direct methods followed by difference Fourier syntheses and then refined by full-matrix least squares against F^2 using SHELXTL [26] with anisotropic thermal parameters for all non-hydrogen atoms. Absorption corrections were applied using SADABS [27]. All H atoms were placed in calculated positions and refined using a riding model. Crystallographic data and refinements are presented in table 1. Relevant interatomic distances and bond angles are collected in table 2, and all the supramolecular interactions in table 3.

Table 1. Crystallographic data and data collection parameters for **1–4**.

Compound	**1**	**2**	**3**	**4**
Empirical formula	$C_{26}H_{18}AgClN_6O_4$	$C_{26}H_{18}AgF_6N_6P$	$C_{27}H_{18}AgF_3N_6O_3S$	$C_{17}H_9Ag_2F_6N_3O_4$
Formula weight	621.78	667.30	671.40	649.01
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Triclinic
Space group (Å °)	*Pbcn*	*Pbcn*	*Pna*2(*1*)	$P\bar{1}$
Units cell dimensions (Å, °)				
a	10.4304(10)	10.7580(8)	14.0039(8)	8.4780(9)
b	18.0044(17)	17.8356(13)	17.6775(10)	10.6648(11)
c	12.9899(12)	13.2329(10)	10.5654(6)	12.3914(13)
α	90	90	90	64.564(2)
β	90	90	90	87.833(2)
γ	90	90	90	70.976(2)
$V/\text{Å}^3$	2439.4(4)	2539.1(3)	2615.5(3)	949.64(17)
Z	4	4	4	2
ρ_{Calcd} (g cm^{-3})	1.693	1.746	1.705	2.270
μ(mm^{-1})	0.983	0.931	0.915	2.152
F(0 0 0)	1248	1328	1344	624
Crystal size (mm)	0.26 × 0.37 × 0.42	0.14 × 0.30 × 0.35	0.10 × 0.30 × 0.32	0.24 × 0.28 × 0.40
θ range for data collection (°)	2.26 to 28.29	2.21 to 28.29	2.25 to 28.25	1.83 to 28.29
Reflections observed	13,439	13,965	14,914	5512
Reflections used [$I > 2\sigma(I)$]	2908	3009	5946	4083
Number of variables	173	182	370	289
Goodness-of-fit on F^2	1.008	1.038	1.011	1.030
Final R_1, wR_2 indices	0.0429, 0.1104	0.0579, 0.1699	0.0314, 0.0699	0.0319, 0.0776

Table 2. Selected interatomic distances (Å) and bond angles (°) for **1–4**.

1	**2**	**3**	**4**
Ag1–N1 2.260(3)	Ag1–N1 2.267(4)	Ag1–N1 2.278(3)	Ag1–N1^a 2.341(3)
Ag1–N2 2.407(3)	Ag1–N2 2.399(4)	Ag1–N2 2.366(2)	Ag1–N2^a 2.418(3)
		Ag1–N4 2.264(3)	Ag1–O2 2.234(3)
N1–Ag1–N2 70.82(1)	N1–Ag1–N2 71.1(2)	Ag1–N5 2.425(3)	Ag1–O4 2.436(2)
N1–Ag1–N1^a 145.7(2)	N1–Ag1–N1^a 141.7(2)		Ag2–N3 2.417(3)
N1–Ag1–N2^a 135.0(1)	N1–Ag1–N2^a 136.7(2)	N1–Ag1–N2 71.0(1)	Ag2–O1 2.253(3)
		N1–Ag1–N5 139.7(1)	Ag2–O3 2.212(3)
		N1–Ag1–N4 137.9(1)	
			N1^a–Ag1–O4 83.8(1)
			N1^a–Ag1–O2 131.0(1)
			N1^a–Ag1–N2^a 69.8(1)
			N3–Ag1–O1 97.0(1)
			N3–Ag1–O3 104.8(1)

Note: ^{a}Symmetry code: **1**a: $-x+2$, y, $-z+3/2$; **2**a: $-x$, y, $-z+1/2$; **4**a: x, $y-1$, z.

3. Results and discussion

3.1. *Synthesis and IR characterization*

The ligand **L** (2-(2′-pyridyl)-quinoxaline), which is soluble in common solvents but not in water, was obtained by literature procedure [16]. By keeping the same solvent systems, the reactions of AgX (X = ClO_4^-, PF_6^-, $CF_3SO_3^-$, or $CF_3CO_2^-$) with **L** in molar ratio of either 1 : 1 or 2 : 1 provided **1–4**; increase of the metal-to-ligand ratio only results in somewhat high yield and better crystal quality of products without change of their

Table 3. Intermolecular distances (Å) and bond angles (°) for **1–4**.

Complex	Supramolecular interaction	Distance	Angle
1	$\pi\cdots\pi^{1\#}$	3.562	
	$\pi\cdots\pi^{2\#}$	3.630	
	$\pi\cdots\pi^{3\#}$	3.612	
2	C11–H11a $\cdots$ F3	3.297	151
	$\pi\cdots\pi^{4\#}$	3.594	
3	$\pi\cdots\pi^{5\#}$	3.661	
	$\pi\cdots\pi^{6\#}$	3.695	
	$\pi\cdots\pi^{7\#}$	3.731	
	$\pi\cdots\pi^{8\#}$	3.815	
	C25–H25a $\cdots$ O1	3.149	130
	C17–H17a $\cdots$ O2	3.181	125
4	Ag2 $\cdots$ O4	2.695	
	Ag1Ag2	3.060	
	C1–H1aO1	3.398	162
	C9–H9aO4	3.332	152

Notes: $^{1\#}$: Centroid distance between rings Ag1–N1–C5–C6–N2 and N2–C6–C7–N3–C8–C13;
$^{2\#}$: Centroid distance between rings Ag1–N1–C5–C6–N2 and C8–C9–C10–C11–C12–C13;
$^{3\#}$: Centroid distance between rings N1–C1–C2–C3–C4–C5 and N2–C6–C7–N3–C8–C13;
$^{4\#}$: Centroid distance between rings Ag1–N1–C5–C6–N2 and C8–C9–C10–C11–C12–C13;
$^{5\#}$: Centroid distance between rings Ag1–N4–C18–C19–N5 and N2–C6–C7–N3–C8–C13;
$^{6\#}$: Centroid distance between rings Ag1–N4–C18–C19–N5 and C8–C9–C10–C11–C12–C13;
$^{7\#}$: Centroid distance between rings Ag1–N1–C5–C6–N2 and N5–C19–C20–N6–C21–C26;
$^{8\#}$: Centroid distance between rings Ag1–N1–C5–C6–N2 and C21–C22–C23–C24–C25–C26.

compositions or structures. Complexes **1**–**4** are air stable and retain their structural integrity at room temperature for one month.

The IR spectra of **1**–**3** show the characteristic absorptions of the quinoxaline ring at 964–966 cm^{-1}, slightly blue shifted by 4–6 cm^{-1} relative to that of the free **L** (960 cm^{-1}) [16]. The appearance of a sharp strong band at 957 cm^{-1} in **4** is characteristic of mixed bidentate–monodentate coordination of the quinoxaline ring, blue-shifted relative to that (*ca* 950 cm^{-1}) of the pure monodentate coordination [28]. The strong bands at 1116, 837, or 1262 cm^{-1} for **1**–**3** are tentatively assigned to the counter-ions (ClO_4^- in **1**, PF_6^- in **2**, and $CF_3SO_3^-$ in **3**). Complex **4** shows asymmetric and symmetric stretching vibrations of $CF_3CO_2^-$ at 1685 and 1538 cm^{-1}, respectively; the difference between ν_{asym}(COO) and ν_{sym}(COO) ($\Delta\nu = 147$ cm^{-1}), smaller than 164 cm^{-1} observed in anionic $CF_3CO_2^-$, reflects its bidentate bridging coordination.

3.2. *Crystal structures*

3.2.1. Ag(L)$_2$•ClO$_4$ (1) and Ag(L)$_2$•PF$_6$ (2). Complexes **1** and **2** consist of a mononuclear cation (as shown in figure 1) and a well-separated ClO_4^- or PF_6^- anion. The Ag^+ has *pseudo*-tetrahedral geometry, with **L** bidentate chelating (Mode I in scheme 1), giving a five-membered ring (Ag1–N1–C5–C6–N2). The Ag–N distances range from 2.260(3) to 2.407(3) Å in **1** and 2.267(4) to 2.399(4) Å in **2**, comparable to Ag–N bond lengths for aromatic nitrogen-donors [2], and longer than the reported Cu(I)–N bond lengths [18] from **L**. The two individually

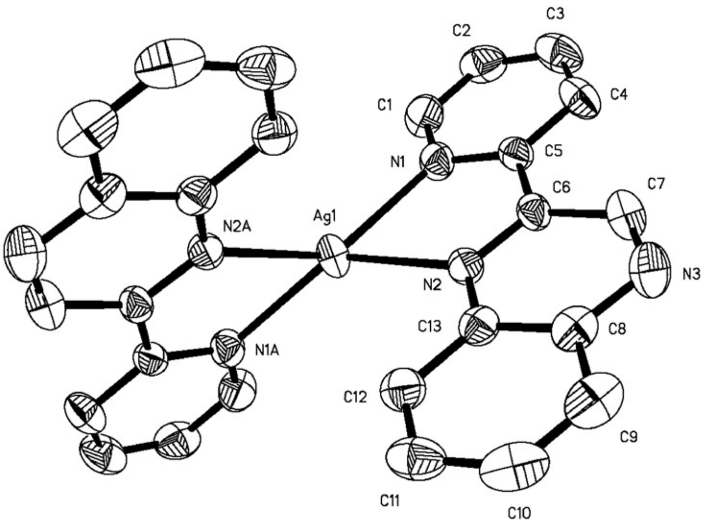

Figure 1. ORTEP of the structure of **1** and **2** with 30% probability ellipsoids; the H-atoms and anions (ClO_4^- or PF_6^-) are omitted for clarity.

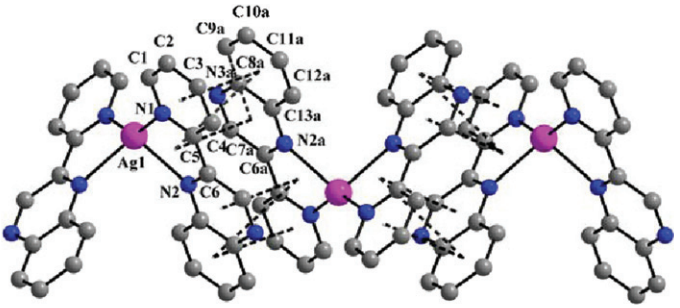

Figure 2. View of the 1-D infinite chain in **1** from $\pi\cdots\pi$ interactions (dash line); the counter-ions ClO_4^- and the H-atoms are omitted for clarity.

planar portions (Ag1–N1–C5–C6–N2) in **1** and **2** are slightly twisted, with the dihedral angles of 3.2° in **1** and 2.2° in **2** smaller than those in Cu(I) [18] or Cu(II) complexes [19] from **L**.

In **1** (figure 2), two adjacent cations are held together with four kinds of complementary $\pi\cdots\pi$ interactions (centroid to centroid distance of 3.562(2)–3.768(2) Å as shown in table 3) resulting in a 1-D infinite chain; ClO_4^- anions do not appear to interact with the host skeleton. Complex **2** is not isostructural to **1** despite the same asymmetrical unit, because of different supramolecular interactions from anions. Adjacent two mononuclear cations of **2** are held together with weak $\pi\cdots\pi$ interactions (3.594 Å) giving the 1-D infinite chain, and the PF_6^- forms weak C11–H11a$\cdots$F3 hydrogen bonds (3.297 Å, 151°), leading to formation of a 2-D layer framework, as shown in figure 3.

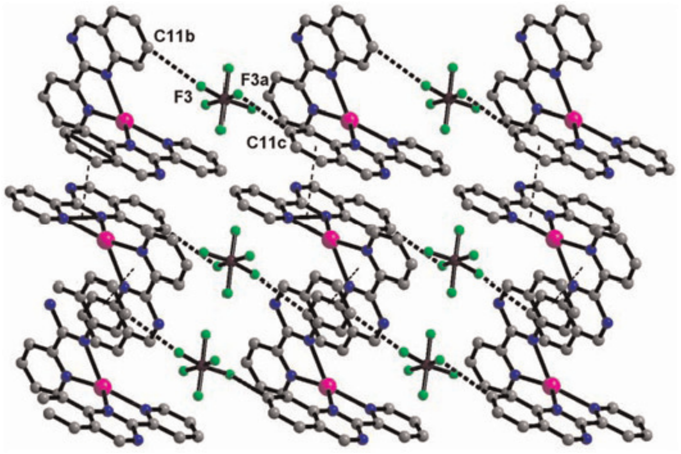

Figure 3. View of the 2-D layer network in **2** from C11–H11a $\cdots$ F3 and $\pi \cdots \pi$ interactions; the H-atoms are omitted for clarity.

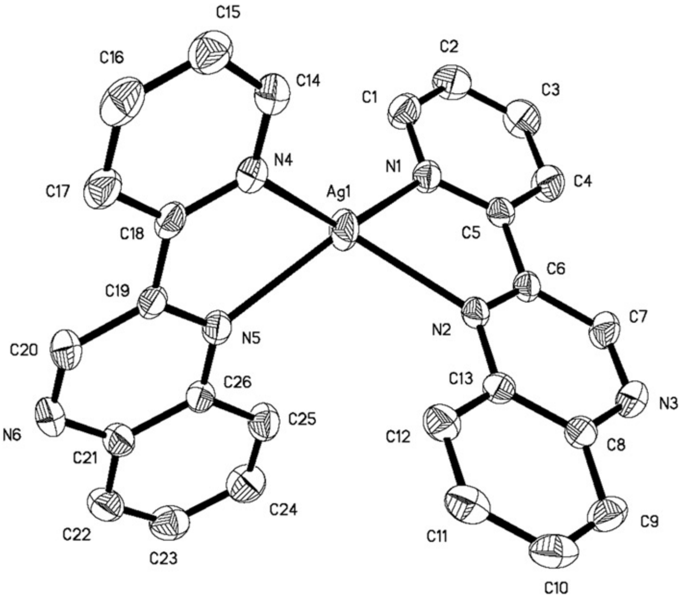

Figure 4. ORTEP of the structure of **3** with 30% probability ellipsoids, the H-atoms and $CF_3SO_3^-$ are omitted for clarity.

3.2.2. Ag(L)$_2$ · CF$_3$SO$_3$ (3). Complex **3** is also mononuclear, with the asymmetric unit consisting of a mononuclear cation and a well-separated $CF_3SO_3^-$ anion, as shown in figure 4. The cation is similar to that in **1** or **2**. The bidentate, chelated mode (Mode I in scheme 1) of **L** in **1**–**3** is comparable to that of the reported Cu(I) [18] or M(II) complexes [19–23], but with slight difference of two planes (pyridine and the quinoxaline ring; two different dihedral angles of 1.8° and 7.2°) from the change of anions in **3**. Figure 5 shows that two adjacent mononuclear cations are linked with four kinds of $\pi \cdots \pi$ interactions [centroid to centroid distance of 3.661(2)–3.815(2) Å as

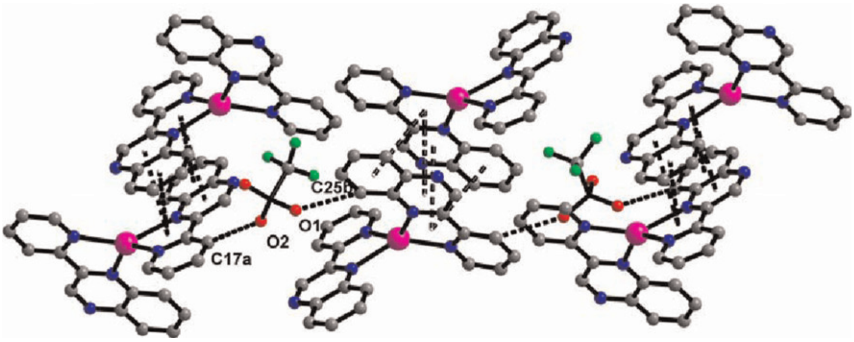

Figure 5. View of 1-D chain framework in **3** from C17–H17···O2, C25–H25 ··· O1 and $\pi \cdots \pi$ interactions; the H-atoms are omitted for clarity.

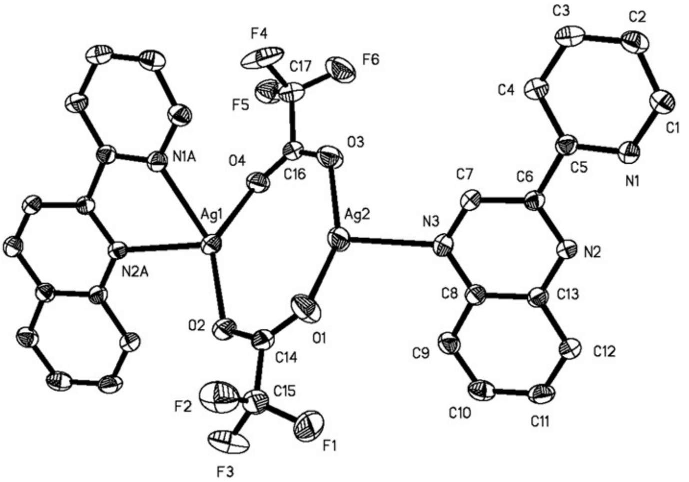

Figure 6. ORTEP drawing of **4** with 30% probability ellipsoids; the H-atoms are omitted for clarity.

shown in table 3] to form a "dimer", resulting in a 1-D infinite chain network connected by two kinds of strong non-classical intermolecular C17–H17a ··· O2 (3.181 Å, 125°) and C25–H25a···O1 (3.149 Å, 130°) hydrogen bonds.

3.2.3. $[AgL(CF_3CO_2)]_n$ (4). With the same procedure as for **1**–**3** except $CF_3CO_2^-$ as anion, a polymeric coordination complex **4** was obtained. As shown in figure 6, the Ag1 has *pseudo*-tetrahedral geometry, consisting of two N donors from pyridine and quinoxaline of one **L** and two O donors from two $CF_3CO_2^-$ anions, while Ag2 shows a trigonal geometry coordinated by one pyridine donor from another **L** and two O donors from two $CF_3CO_2^-$ anions. The two bridged $CF_3CO_2^-$ anions connect adjacent two coordinated **L** in head-to-tail fashion (mixed bidentate–monodentate mode II [25] of **L** as shown in scheme 1) to obtain the 1-D infinite linear chain with short Ag1 ··· Ag2 contact (3.060 Å). For two bridging $CF_3CO_2^-$ and short Ag1 ··· Ag2 contacts, two linear chains interacted from weak Ag2 ··· O4 (2.065 Å) interaction and complementary C9–H9a ··· O4 (3.332 Å, 152°) intermolecular supramolecular interactions forming an

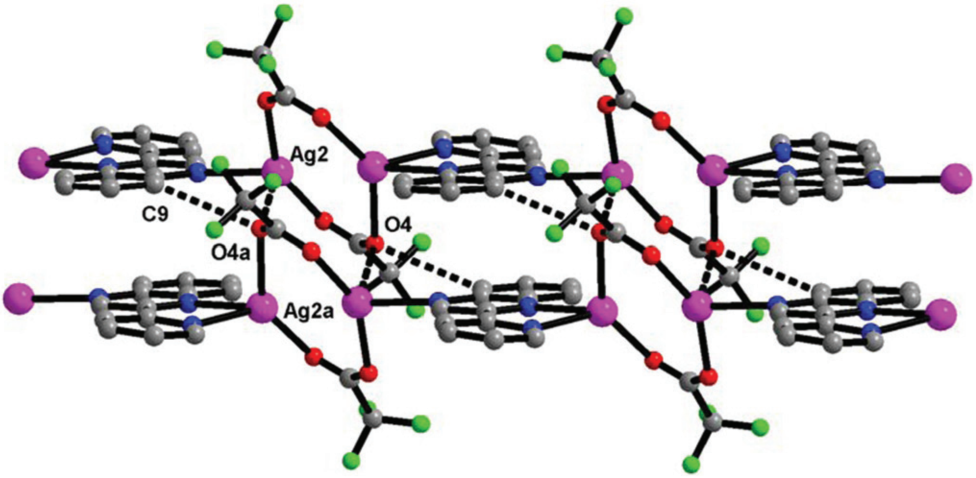

Figure 7. View of the 1-D double chain in **4** from C9–H9 $\cdots$ O4 and Ag2 $\cdots$ O4 interactions; the H-atoms are omitted for clarity.

infinite 1-D double chain framework, as shown in figure 7. Adjacent two double chains are held parallel to each other resulting in the 2-D non-interpenetrating network shown in figure 8, from intermolecular C1–H1a $\cdots$ O1 (3.398 Å, 162°) hydrogen bonds.

3.2.4. Effect of counter-ions on structures. Variation of the anion in **1**–**3** leads to the same mononuclear $[AgL_2]^+$ cation, even with excess Ag^+, due to the formation of stable five-membered chelating ring (Ag1–N1–C5–C6–N2). Different anions lead to different weak supramolecular interactions. In **1**, ClO_4^- is just a counter-ion, not supporting the supramolecular structure, while weak C–H $\cdots$ X (X = F or O) hydrogen bonds from PF_6^- or $CF_3SO_3^-$ in **2** and **3** affect the connection of adjacent mononuclear $[AgL_2]^+$ cations, influencing their supramolecular structures. For **4**, secondary five-membered chelation effect (Ag1–O2–C14–O1–Ag2 or Ag1–O4–C16–O3–Ag2) from the counter-ion $CF_3CO_2^-$, with stronger coordination than the anions of **1**–**3** or the NO_3^- in 1-D $[AgL(NO_3)]_n$ [25], gives two different coordination geometries (*pseudo*-tetrahedral and trigonal) of Ag^+ (coordination mode II of **L**) and templates the polymeric system with the short Ag $\cdots$ Ag contacts and complicated supramolecular interactions, evident in the tighter stacking of 1-D double chains and the formation of the 2-D non-interpenetrating network for **4**.

4. Summary

The syntheses and structures of four silver(I) complexes of 2-(2′-pyridyl)-quinoxaline (**L**), with ClO_4^-, PF_6^-, $CF_3SO_3^-$, and $CF_3CO_2^-$ as counter-ions, are reported. Coordination ability and tendency to enter into weak supramolecular interactions by the anions provided different supramolecular arrays. Fabrication of molecular

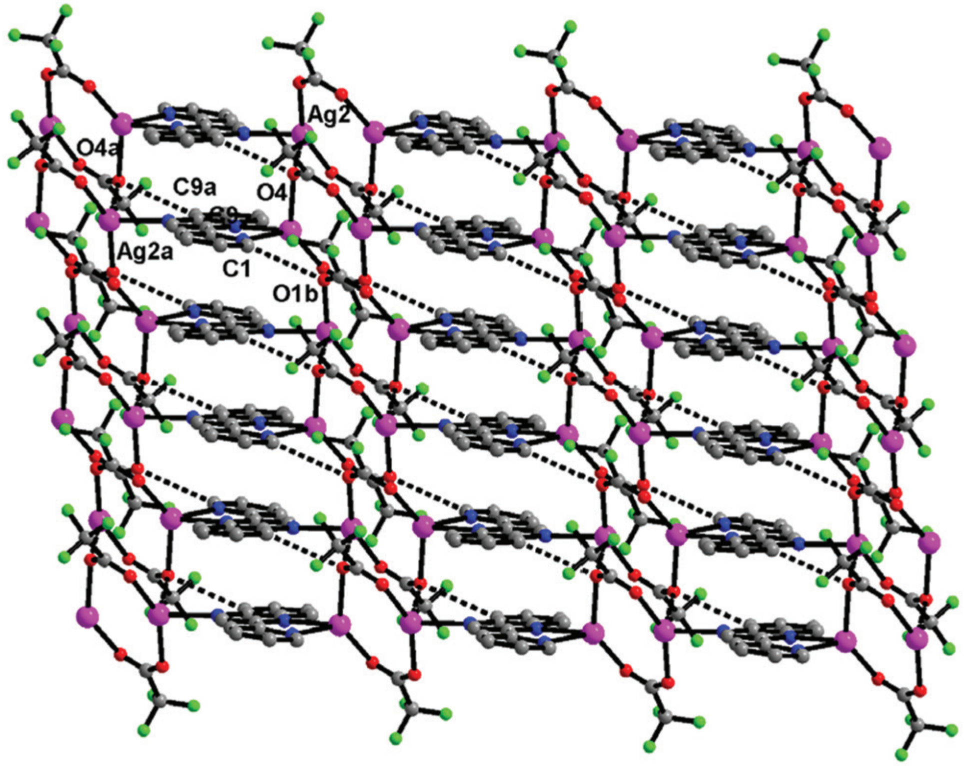

Figure 8. View of stacking of three adjacent double chains in **4** from C1–H1 ··· O1 interactions; the H-atoms are omitted for clarity.

architectures from **L** with coordination mode III will be a challenge and work is now underway.

Supplementary material

Additional crystallographic details and complete listings for the structures reported have been deposited with the Cambridge Crystallographic Data Center (CCDC) with CCDC Nos. 645165 for **1**, 645166 for **2**, 645167 for **3** and 645168 for **4**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax:+44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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