Syntheses and Structural Characterization of Ag^{I} Complexes with the *N*,*N*′-Di(2-pyridyl)oxamide Ligand

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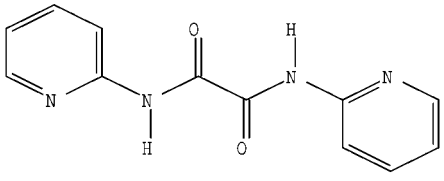
Keywords: Silver / Nitrogen heterocycles / Coordination polymers / Trinuclear complexes

A series of the silver(I) complexes $\{[Ag(\mathbf{L})][NO_3]\}_\infty$ (**1**), $\{[Ag(\mathbf{L})(CH_3CN)][ClO_4]\}_\infty$ (**2**), $\{[Ag_2(\mathbf{L})_3(CH_3CN)_2][PF_6]_2\}_\infty$ (**3**), and $[Ag_3(\mathbf{L})_4(CH_3CN)_4][BF_4]_3$ (**4**) [where **L** = *N*,*N*′-di(2-pyridyl)oxamide] have been prepared by the reactions of AgX (X = NO_3^-, ClO_4^-, PF_6^- and BF_4^-) with **L**. All the complexes have been structurally characterized by X-ray crystallography, confirming that **1**–**3** are coordination polymers whereas **4** is a trinuclear complex. Complex **1** forms helical chains which are interlinked through a series of Ag···O interactions and C–H···O hydrogen bonds. In complexes **2** and **3**, a new set of interactions involving two Ag···O interactions and self-complementary double N–H···O hydrogen bonds were found to link the linear chains and ladder structures into polymer pairs (for **2**) and molecular sheets (for **3**). In complex **4**, the molecules are interlinked by extensive Ag···N interactions and π–π stacking interactions to form molecular bands.

Introduction

Recently, a great deal of effort has been devoted to the self-assembly of organic and inorganic molecules in the solid state, because it extends the range of new solids which can be designed to have particular physical and chemical properties.[1] Among the various types of interactions employed to create larger molecular arrays, covalent and hydrogen bonds are the most widely used.[2] The use of metal ions to link organic molecules is an alternative method for the design of inorganic supramolecules. The range and variety of self-assembling inorganic structures that can be constructed relies on the presence of suitable metal−ligand interactions and hydrogen bonds. We have recently reported the self-assembly of molecules through N−H···Cl[3a] and N−H···Br[3a] interactions.

Many topologically promising Ag^{I}-containing architectures have been constructed with nitrogen-containing bidentate building blocks.[4] These polymers include 1-D, 2-D and 3-D network structures.[4b] Despite some recent progress, the ability to predict and control the supramolecular assembly of molecules remains elusive, and much more work is required to understand the inter- and intramolecular forces that determine the patterns of molecular structure and crystal packing in the solid state. During our study on the reactions of Ag^{I} ion with the bidentate ligand *N*,*N*′-di(2-pyridyl)oxamide (**L**), (which contains both amide and pyridyl groups) we found that it can form coordination polymers capable of self-assembling into 2-D molecular structures through a series of interactions involving Ag···O weak covalent bonds and self-complementary double N−H···O hydrogen bonds.[5] It was also found that changing the counterion of Ag^{I} had a drastic effect on the structures of the Ag^{I} coordination polymer. The syntheses and structural characterization of Ag^{I} complexes of the types $\{[Ag(\mathbf{L})][NO_3]\}_\infty$, $\{[Ag(\mathbf{L})(CH_3CN)][ClO_4]\}_\infty$, $\{[Ag_2(\mathbf{L})_3(CH_3CN)_2][PF_6]_2\}_\infty$ and $[Ag_3(\mathbf{L})_4(CH_3CN)_4][BF_4]_3$ form the subject of this report.



L

Results and Discussion

Syntheses

The ligand *N*, *N*′-di(2-pyridyl)oxamide (**L**) was prepared by reaction of 2-aminopyridine and oxalyl chloride in CH_2Cl_2, in accordance with a literature procedure.[6] The reactions of **L** with AgX (X = NO_3^-, ClO_4^-, PF_6^- and BF_4^-) in refluxing CH_3CN afforded the complexes $\{[Ag(\mathbf{L})][NO_3]\}_\infty$ (**1**), $\{[Ag(\mathbf{L})(CH_3CN)][ClO_4]\}_\infty$ (**2**), $\{[Ag_2(\mathbf{L})_3(CH_3CN)_2][PF_6]_2\}_\infty$ (**3**) and $[Ag_3(\mathbf{L})_4(CH_3CN)_4][BF_4]_3$ (**4**), respectively. All these complexes were structurally characterized by X-ray crystallography. Complexes **1**−**4** were insoluble in most organic solvents; crystals suitable for X-ray diffraction studies were obtained by layering their CH_3CN solutions with diethyl ether.

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Structure of the Ligand L

The crystal structure of the ligand belongs to the space group $P4bar2_1/c$ with eight molecules in each unit cell. Figure 1 shows the packing of these molecules. It can be seen that the ligand forms one dimensional chains in the solid state, and the molecules are held together by a series of donor-acceptor-donor-acceptor (DADA) quadruple hydrogen bonds and donor-acceptor (DA) double hydrogen bonds. The one dimensional chains interact with each other through extensive C−H···O interactions (H···O: 2.576 Å; ∠ C−H···O: 149.9°). The centrosymmetric DADA:ADAD self-complementary interaction involves two strong N−H···N and two weak C−H···O hydrogen bonds. The H···N distance in the N−H···N interaction is 2.220 Å, with an N−H···N angle of 153.2°, whereas the H···O distance in the C−H···O interaction is 2.451 Å, with a C−H···O angle of 121.3°. The centrosymmetric DA:AD double hydrogen bonds involve two N−H···N interactions; the H···N distance and N−H···N angle are 2.203 Å and 161.5°, respectively. Noticeably, this DADA:ADAD system involves two N−N, two N−C, and two N−C secondary interactions,[5c] which are all repulsive. This system is in marked contrast to the DADA:ADAD system (which has two strong N−H···N and two strong O−H···O interactions) found for 6-methyl-2-butylureidopyrimidone, in which four N−N and two N−O repulsive secondary interactions were observed.[7]

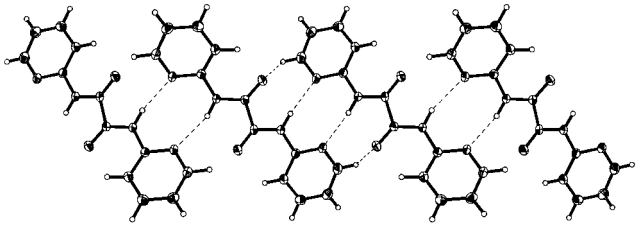

Figure 1. An ORTEP diagram of **L** showing the interactions among the ligands

Structure of 1

The single-crystal X-ray structure of complex **1** shows that the silver atom is bound to the nitrogen atoms of two symmetry-related **L** ligands [Ag−N(2): 2.183 (4), Ag−N(5A): 2.198 (3) Å] in a distinctly non-linear geometry [N(2)−Ag−N(5A): 154.95(13)°]. Selected bond lengths and angles are listed in Table 1. As illustrated in Figure 2 (a), the asymmetric unit of **1** consists of one [Ag(**L**)][NO_3] subunit, which under an appropriate symmetry operation produces the polymeric structure, Figure 2 (b). It is interesting to note that the bidentate ligand **L** in each cation is not flat, but twisted around the C−N bond, with a dihedral angle of 47.0° between the planes of the two pyridine rings, resulting in a series of single-twist helicates. Each single-twist helix contains two Ag^I−**L** units, as shown in Figure 2 (b). The helical chains are interlinked through a series of Ag···O−C (Ag···O: 3.567 Å) interactions and C−H···O (H···O = 2.555 Å, ∠ C−H−O: 144.2°) hydrogen bonds. The nitrate ions form bridges between adjacent chains through all three oxygen atoms [Figure 2 (c)] and link the cations through a series of Ag···O interactions (Ag···O: 2.695−3.336 Å) and N−H···O (H···O: 2.280 and 2.296 Å, ∠ N−H···O: 140.3 and 162.1°, respectively) hydrogen bonds. In addition to the weak interactions mentioned above, the **L** ligands in each helix experience π−π interactions, with interplanar distances of 3.905 Å between the pyridine rings.

Table 1. Selected bond lengths (Å) and angles (°) for complexes **1**−**4**

Complex **1**			
Ag−N(2)	2.183(4)	Ag−N(5A)	2.198(3)
N(2)−Ag−N(5A)	154.95(13)		
Complex **2**			
Ag(1)−N(3)	2.168(4)	Ag(1)−N(2)	2.188(4)
Ag(2)−N(7)	2.300(4)	Ag(2)−N(6)	2.305(4)
Ag(2)−N(9)	2.360(5)	Ag(2)−N(10)	2.372(5)
N(3)−Ag(1)−N(2)	164.29(14)	N(7)−Ag(2)−N(6)	145.13(14)
N(7)−Ag(2)−N(9)	97.30(17)	N(6)−Ag(2)−N(9)	103.24(16)
N(7)−Ag(2)−N(10)	103.68(17)	N(6)−Ag(2)−N(10)	98.77(17)
N(9)−Ag(2)−N(10)	103.1(2)		
Complex **3**			
Ag−N(3)	2.268(2)	Ag−N(1)	2.279(2)
Ag−N(5)	2.504(2)	Ag−N(7)	2.550(3)
N(3)−Ag−N(1)	150.12(8)	N(3)−Ag−N(5)	111.59(8)
N(1)−Ag−N(5)	92.36(8)	N(3)−Ag−N(7)	95.51(9)
N(1)−Ag−N(7)	102.01(9)	N(5)−Ag−N(7)	90.75(10)
Complex **4**			
Ag(1)−N(1)	2.257(5)	Ag(1)−N(9)	2.428(7)
Ag(2)−N(10)	2.220(6)	Ag(2)−N(5)	2.296(4)
Ag(2)−N(4)	2.298(5)		
N(1A)−Ag(1)−N(1)	125.4(2)	N(1A)−Ag(1)−N(9)	121.35(19)
N(1)−Ag(1)−N(9)	99.32(19)	N(1A)−Ag(1)−N(9A)	99.32(19)
N(1)−Ag(1)−N(9A)	121.35(19)	N(9)−Ag(1)−N(9A)	83.8(3)
N(10)−Ag(2)−N(5)	109.57(18)	N(10)−Ag(2)−N(4)	83.8(3)
N(5)−Ag(2)−N(4)	116.57(18)		

Structure of 2

The asymmetric unit and infinite molecular structure of **2** are depicted in Figure 3 (a and b), respectively. Selected bond lengths and angles are listed in Table 1. Figure 3 (b) shows that **2** is a coordination polymer of [Ag(**L**)(CH_3CN)][ClO_4]. The Ag metal centres possess two types of geometries. One has a distorted tetrahedral geometry in which two CH_3CN ligands and two **L** ligands coordinate to the metal centre, whereas the other has an approximately linear geometry [N(3)−Ag(1)−N(2): 164.29(14)°] in which the metal is coordinated by two **L** ligands. The largest N(7)−Ag(2)−N(6) angle is 145.13(14)°, whereas the remaining five angles are in the range 97.30(17) to 103.68 (17)°. The bidentate **L** ligand in each cation is not

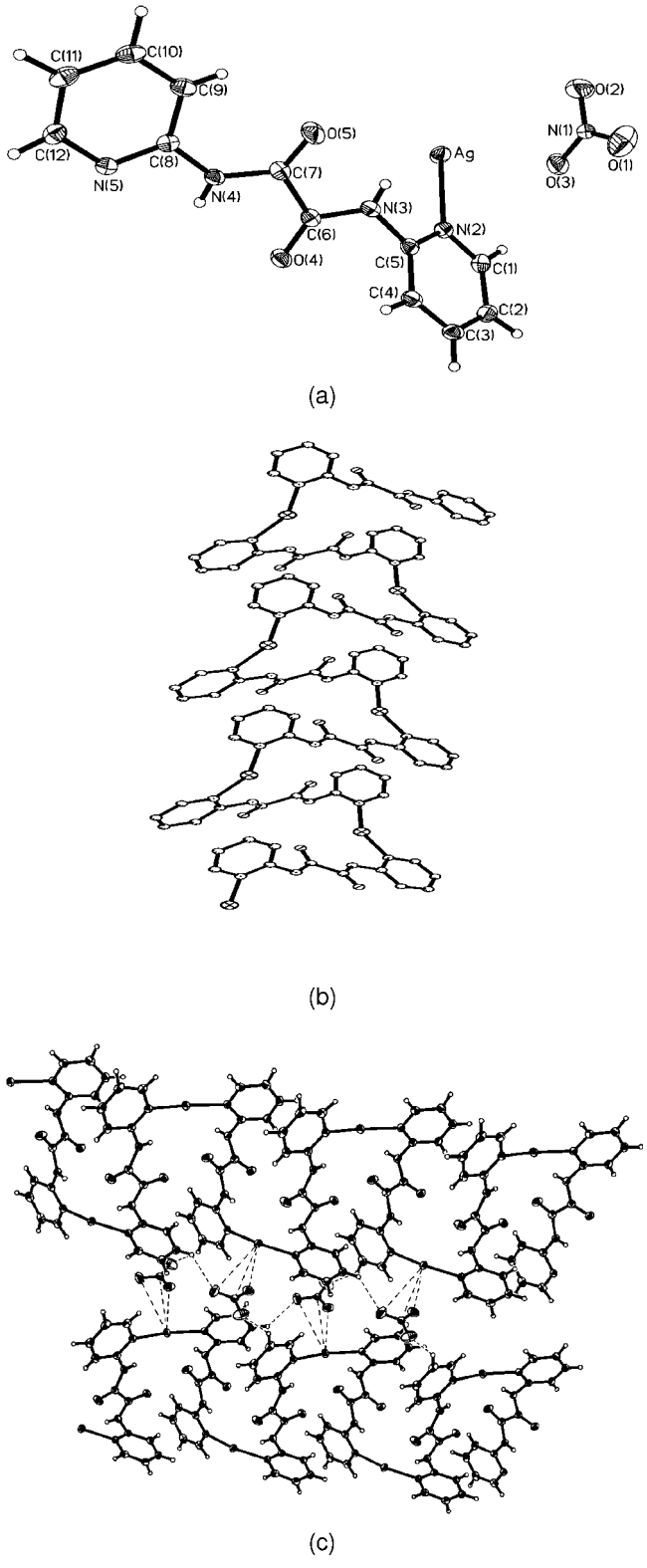

Figure 2. (a) The asymmetric unit of **1**; (b) an ORTEP diagram showing the helical structure of **1**; the hydrogen atoms are omitted for clarity; (c) the interactions between the anions and the cations

flat, but twisted around the C−N bonds, with a dihedral angle of 31.7° between the planes of the two pyridine rings. Most interestingly, each polymer chain is linked to the other through a series of self-complementary double hydrogen bonds and Ag···O interactions (Ag···O: 3.194 and 3.047 Å) to form polymer pairs. The DA:AD self-complementary interaction involves two strong N−H···O hydrogen bonds. The H···N distances are 2.474 and 2.422 Å and the corresponding angles are 132.6 and 141.4°, respectively. One of the ClO_4^- anions interacts with the methyl hydrogen of the CH_3CN ligand through two C−H···O hydrogen bonds (H···O: 2.302 and 2.544 Å and ∠ C−H−O: 139.5 and 133.3°, respectively); the other ClO_4^- anion interacts with the metal centre through a Ag···O interaction (Ag···O: 2.739 Å). The molecules are further linked through intermolecular π−π interactions, with interplanar distances of 3.859 Å between the pyridine rings.

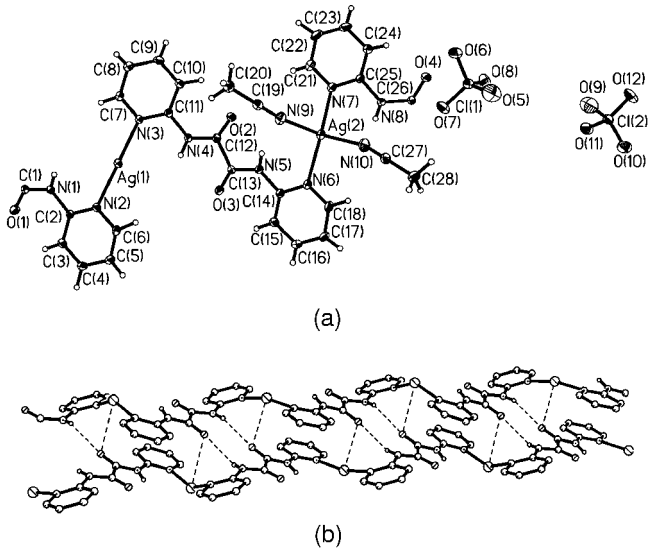

Figure 3. (a) The asymmetric unit of **2**; (b) the interactions between the cations; the pyridine hydrogen atoms are omitted for clarity

Structure of 3

The asymmetric unit of **3** is depicted in Figure 4 (a), and selected bond lengths and angles are listed in Table 1. The single-crystal X-ray structure of **3** shows that it is a coordination polymer consisting of $Ag_4(\mathbf{L})_4(CH_3CN)_2$ metallacycles, and forming a ladder-type structure [Figure 4 (b)]. The distorted tetrahedral coordination geometry of the Ag^I metal centre involves one CH_3CN ligand and three **L** ligands. The ladders are interlinked to each other through a series of self-complementary double N−H···O hydrogen bonds and Ag···O interactions (Ag···O: 3.085 Å) to form molecular sheets. The H···O distance in the strong N−H···O interaction is 2.290 Å, with an N−H−O angle of 161.6°. The PF_6^- anions interact with the pyridyl hydrogen atoms of the **L** ligands through C−H···F hydrogen bonds (H···F: 2.542 and 2.508 Å, with angles 143.4 and 152.7°, respectively). In marked contrast to the twisted conformations in complexes **1** and **2**, the bidentate **L** ligand in each cation of complex **3** is flat, with a dihedral angle of 0° between the planes of the two pyridine rings.

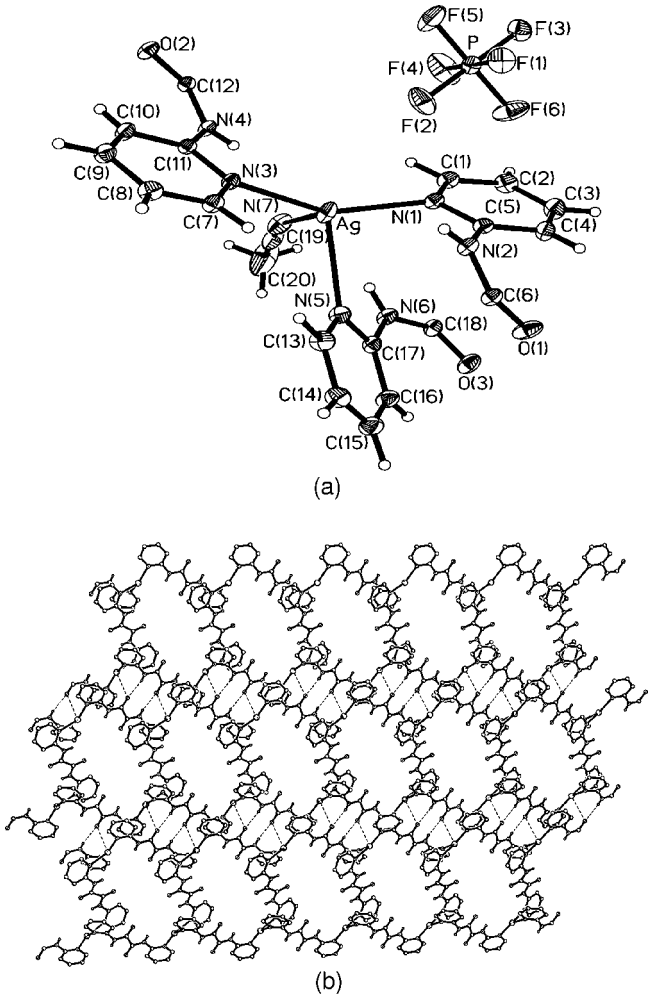

Figure 4. (a) The asymmetric unit of **3**; (b) an ORTEP diagram showing the ladder type structure of **3**; the CH_3CN molecules and the pyridyl hydrogen atoms are omitted for clarity

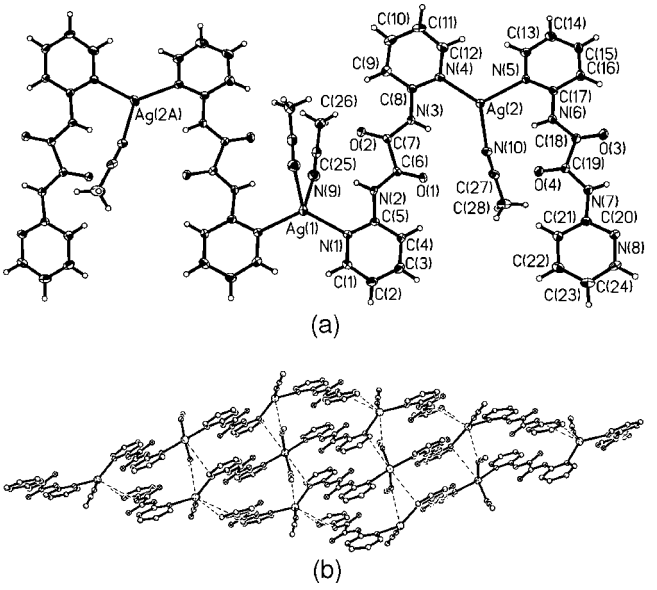

Figure 5. (a) An ORTEP diagram of **4**; (b) an ORTEP diagram showing the interactions among the molecules of **4**; the hydrogen atoms are omitted for clarity

In the structures of complexes **2** and **3**, a new set of interactions involving a pair of Ag···O interactions and self-complementary double N−H···O hydrogen bonds was found to self-assemble the coordination polymers into 2-D networks. By way of comparison, the complementary amide hydrogen bonds in the complexes $\{[AgL']X\}_\infty$ [L′ = *N*,*N*′-bis(3-pyridinecarboxamido)-1,2-ethane; X = ClO_4^-, $CF_3SO_3^-$ or NO_3^-][8] show H···O distances in the range 2.833 to 2.970 Å, which are significantly longer that those found for complexes **2** and **3** (2.290 to 2.474 Å).

Structure of 4

The ORTEP diagram of the trinuclear complex **4** and its packing diagram are depicted (see a and b in Figure 5), respectively. Selected bond lengths and angles are listed in Table 1. The single-crystal X-ray structure of **4** shows that the complex consists of a trinuclear cation $[Ag_3(\mathbf{L})_4(CH_3CN)_4]^{3+}$ and three BF_4^- anions. Two types of coordination geometries are observed for the metal centres. The Ag[I] ion, which is coordinated by two **L** ligands and one CH_3CN ligand, has a distorted triangular planar geometry, whereas the other, coordinated by two **L** and two CH_3CN ligands, has a distorted tetrahedral geometry. The dihedral angles between the planes of the two pyridine rings are 2.0 and 5.2°. The molecule is chiral with a C_2 axis bisecting the N(9)−Ag(1)−N(9A) angle. The trinuclear complexes are interlinked to each other through extensive Ag···N (Ag···N: 3.487 and 3.654 Å) and π−π stacking interactions to form molecular bands. These are interlinked by the BF_4^- anions through extensive C−H···F hydrogen bonds. The interplanar distances between the pyridine rings forming the π−π stacking interactions are 3.875, 3.619 and 3.783 Å, respectively.

In the four complexes mentioned above, the silver atoms of complexes **2**, **3** and **4** have distorted tetrahedral geometries, presumably due to the ligand constraints. Complex **3** has the greatest distortions, with the angles in the range 90.75(10) to 150.12(8)°. In complexes **2** and **4**, the tetrahedral silver atoms show a smaller degree of distortion, with angles in the range 97.30(17) to 145.13(14)° for **2** and 83.8(3) to 125.4(2)° for **4**.

Concluding Remarks

In this study, the coordination chemistry of AgX (X = NO_3^-, ClO_4^-, PF_6^- and BF_4^-) with *N*,*N*′-di(2-pyridyl)oxamide was investigated. Complex **1** is a coordination polymer which forms helical chains whereas complex **4** is a discrete trinuclear complex. In complexes **2** and **3**, a new set of interactions involving two Ag···O interactions and self-complementary double N−H···O hydrogen bonds was found, which link the linear chains and ladder structures of **2** and **3** into polymer pairs and molecular sheets, respec-

tively. Obviously, the *N*,*N*′-di(2-pyridyl)oxamide ligand is sufficiently flexible to adjust to the stereochemical requirements for the formation of complexes **1**−**4** by twisting about the C−N bonds. It is also shown that the self-assembly frameworks of these Ag^I coordination polymers can be altered by changing their counterions. These frameworks are also highly influenced by coordination of CH_3CN solvent molecules to the Ag^I centres.

Experimental Section

General Procedures: All manipulations were carried out under dry, oxygen-free nitrogen by using Schlenk techniques, unless otherwise noted. Solvents were dried and deoxygenated by refluxing over the appropriate reagents before use. *n*-Hexane and diethyl ether were purified by distillation from sodium/benzophenone, dichloromethane from P_2O_5, and acetonitrile from CaH_2. The visible absorption spectra were recorded on a Hitachi U-2000 spectrophotometer. IR spectra were obtained from a Jasco FT/IR-460 plus spectrometer. Elemental analyses were obtained from a PE 2400 series II CHNS/O analyzer or a HERAEUS VaruoEL analyzer.

Materials: The reagents AgX (X = NO_3^-, ClO_4^-, BF_4^- and PF_6^-) were purchased from Aldrich Chemical Co. The ligand *N*, *N*′-di(2-pyridyl)oxamide was prepared according to a literature procedure.[6]

Syntheses: The complexes were synthesized by reaction of AgX (X = NO_3^-, ClO_4^-, PF_6^- and BF_4^-) with *N*, *N*′-di(2-pyridyl)oxamide in CH_3CN.

$[Ag(L)(NO_3)]_\infty$ (1): $AgNO_3$ (0.050 g, 0.294 mmol) and *N*,*N*′-di(2-pyridyl)oxamide (0.142 g, 0.587 mmol) were added successively to a flask containing 15 mL of CH_3CN. The mixture was then refluxed for 24 h to yield a yellow solution, and diethyl ether added to induce precipitation. The precipitate was filtered and washed with diethyl ether and then dried under reduced pressure to give the light yellow product. Yield: 0.087 g (72%). UV/Vis (CH_3CN): λ = 299 nm. IR (KBr disk): ν̃ = 3168 (br), 1686 (s), 1592 (m), 1574 (m), 1497 (m), 1432 (s), 1384 (m), 1302 (m), 1152 (w), 777 (w), 553 (w) cm^{-1}. $C_{12}H_{10}AgN_5O_5$ (412.12): calcd. C 34.97, H 2.44, N 16.99; found C 35.01, H 2.20, N 17.01.

$[Ag(L)(CH_3CN)(ClO_4)]_\infty$ (2): Prepared as described for **1**. Yield: 65%. UV/Vis (CH_3CN): λ = 282 nm. IR (KBr disk): ν̃ = 3164 (br), 1686 (s), 1592 (m), 1575 (m), 1497 (m), 1433 (s), 1302 (m), 1087 (m), 778(w), 625(w), 552(w), 483(w), 418(w) cm^{-1}. $C_{28}H_{26}Ag_2Cl_2N_{10}O_{12}$ (981.23): calcd. C 34.27, H 2.67, N 14.27; found C 34.67, H 2.28, N 14.28.

$[Ag_2(L)_3(CH_3CN)_2(PF_6)_2]_\infty$ (3): Prepared as described for **1**. Yield: 58%. UV/Vis (CH_3CN): λ = 314 nm. IR (KBr disk): ν̃ = 3167 (br), 1685 (s), 1574 (m), 1497 (m), 1433 (s), 1302 (m), 1151 (w), 842 (m), 779 (w), and 559 (w) cm^{-1}. $C_{44}H_{46}Ag_2F_{12}N_{14}O_7P_2$ (1388.60): calcd. C 38.06, H 3.34, N 14.12; found C 38.05, H 3.10, N 14.16.

Preparation of $[Ag_3(L)_4(CH_3CN)_4][BF_4]_3$ (4): Prepared as described for **1**. Yield: 89%. UV/Vis (CH_3CN): λ = 306 nm. IR (KBr disk): ν̃ = 3164 (br), 1686 (s), 1592 (m), 1575 (m), 1497 (m), 1433 (s), 1302 (m), 1051(m), 779 (m), 552 (w) cm^{-1}. $C_{56}H_{52}Ag_3B_3F_{12}N_{20}O_8$ (1717.22): calcd. C 39.17, H 3.05, N 16.31; found C 39.55, H 3.08, N 16.35.

X-ray Crystallography: The diffraction data of **1** was collected with a Bruker AXS diffractometer, which was equipped with graphite-monochromated Mo-K_α (0.71073 Å) radiation. Data reduction was carried by standard methods with use of well-established computational procedures.[9] Basic information pertaining to crystal parameters and structure refinement is summarized in Table 2. The structure factors were obtained after Lorentz and polarization cor-

Table 2. Crystal data for the ligand **L** and compounds **1**−**4**

Compound	**L**	**1**	**2**	**3**	**4**
Empirical formula	$C_{12}H_{10}N_4O_2$	$C_{12}H_{10}AgN_5O_5$	$C_{28}H_{26}Ag_2Cl_2N_{10}O_{12}$	$C_{22}H_{23}AgF_6N_7O_{3.5}P$	$C_{56}H_{52}Ag_3B_3F_{12}N_{20}O_8$
Formula mass	242.24	412.12	981.23	694.31	1717.22
Crystal system	tetragonal	monoclinic	triclinic	triclinic	monoclinic
Space group	$P4bar2_1/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a, Å	13.355(2)	10.578(1)	8.354(2)	9.121(1)	32.198(8)
b, Å	13.355(2)	9.237(1)	13.583(3)	12.456(2)	13.949(2)
c, Å	13.160(1)	14.705(1)	15.951(6)	13.443(2)	16.092(3)
α,°	90	90	104.49(3)	108.012(10)	90
β,°	90	104.915(5)	95.21(3)	103.289(9)	115.681(13)
γ,°	90	90	95.96(2)	105.532(12)	90
V, Å^3	2347.2(5)	1388.5(2)	1730.1(9)	1315.4(3)	6514(2)
Z	8	4	2	2	4
$D_{calcd.}$, g/cm^3	1.371	1.971	1.884	1.753	1.751
Crystal size, mm	0.2 × 0.4 × 0.2	0.1 × 0.8 × 0.1	0.1 × 0.4 × 0.1	0.4 × 0.4 × 0.4	0.1 × 0.8 × 0.2
μ(Mo-K_α), mm^{-1}	0.098	1.488	1.364	0.912	0.998
T, °C	25	25	25	25	25
Data/restraints/parameters	1428/0/204	2450/0/248	5986/0/567	4466/0/437	5727/3/477
Quality-of-fit indicator[a]	1.000	1.062	1.035	1.063	1.014
Final *R* indices [$I > 2\sigma(I)$][b] [c]	R_1 = 0.0418	*R*1 = 0.0381	*R*1 = 0.0408	*R*1 = 0.0308	*R*1 = 0.0591
	wR_2 = 0.0801	*wR*2 = 0.0918	*wR*2 = 0.1111	*wR*2 = 0.0787	*wR*2 = 0.1323
R indices (all data)	R_1 = 0.082	*R*1 = 0.0526	*R*1 = 0.0508	*R*1 = 0.0350	*R*1 = 0.1114
	wR_2 = 0.0943	*wR*2 = 0.0997	*wR*2 = 0.1207	*wR*2 = 0.0823	*wR*2 = 0.1610

[a] Quality-of-fit = $[\Sigma w(F_o^2 - F_c^2)^2/N_{observed} - N_{parameters})]^{1/2}$. [b] $R1 = \Sigma F_o - F_c/\Sigma F_o$. [c] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (ap)^2 + (bp)]$, $p = [\max.(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$. **L**: $a = 0.0401$, $b = 0.000$; **1**: $a = 0.0499$, $b = 1.3564$; **2**: $a = 0.0651$, $b = 3.3187$; **3**: $a = 0.0362$, $b = 1.2567$; **4**: $a = 0.0624$, $b = 24.1437$

rections. The positions of the heavy atoms, including the silver atoms, were located by the direct method. The remaining atoms were found in a series of alternating difference Fourier maps and least-square refinements.[10] The final residuals were $R_1 = 0.0381$, $wR2 = 0.0918$. The crystallographic procedures for **2**−**4** were similar to those for **1**. Basic information pertaining to crystal parameters and structure refinement is summarized in Table 2.

CCDC-219402 to -219406 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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