Dynamic ring-opening polymerization of silver(I) complexes with bis(amidopyridine) ligands[†]

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The factors which influence the formation of chelate, macrocycle or polymer in the reaction of silver(1) salts with bis(pyridine) ligands have been probed by studying structures in the solid state and cold spray ionization mass spectra in solution, with the ligands C_6H_4 -1,3-[CONR(CH₂)_n-3- C_3H_4N]₂, 1 (R = Me, n = 0) or 3 (R = H, n = 1) or 5-*t*-Bu- C_6H_3 -1,3-[CONR(CH₂)_n-4- C_5H_4N]₂, 2 (R = Me, n = 0) or 4 (R = H, n = 1). In both the solid state and solution, the complex [Ag(1)₂]BF₄ exists as a chelate complex 5. The ligands NN = 2-4 form complexes in the solid state with either macrocyclic structures [Ag₂(μ -NN)₂]X₂ [6, NN = 2, X = BF₄; 9, NN = 3, X = NO₃] or polymeric structures [7, NN = 2, X = NO₃; 8, NN = 3, X = CF₃CO₂; 10, NN = 4, X = CF₃CO₂]. The ligands 2 and 3 gave both macrocyclic and polymeric complexes, depending on the anion. In solution, these complexes existed as mixtures of macrocycles and ring-opened oligomers. In the crystalline state, the complexes 6-10 underwent supramolecular association through combinations of hydrogen bonding, secondary bonding of the type Ag \cdots X to anions, or argentophilic bonding of the type Ag \cdots Ag.

Introduction

There is much current interest in the self-assembly of coordination polymers, whose topology may be controlled by the stereochemistry of the metal ion and the geometry of the ligand.¹ The chemistry of silver(I) has played a leading role in this field, in part because silver(I) forms labile metal-ligand bonds which can take part in dynamic coordination chemistry.¹⁻³ In addition, silver(I) can adopt several different coordination geometries, and so it has yielded a particularly rich array of supramolecular structures.¹⁻⁶ Coordination polymers containing amide functionality can give higher order structures because hydrogen bonding through the amide functionality can complement the dynamic coordination chemistry in forming polymeric networks through self-assembly.⁴⁻⁶ If the ligands are flexible, it is sometimes possible to control the ring-opening polymerization by either kinetic or thermodynamic control,⁴⁻⁶ and an example from silver(I) chemistry is shown in Scheme 1.6 The macrocycle A to polymer B equilibrium involves reversible dissociation of Ag-N bonds and reversible changes in conformation of the N-methylamide groups.

Characterization of the fascinating architectures of coordination polymers mainly depends on solid state characterization using X-ray crystallography. In the solution state, spectroscopic analysis by IR, NMR and ESI-MS may be used, but it is often very difficult to determine if the observed solid state polymeric structure is maintained in solution.¹⁻⁷ For example, the value of NMR spectroscopy is limited because of dynamic effects if there is an easy equilibrium between macrocyclic and linear units in solution.⁷ The standard form of ESI-MS has proved to be a useful method for identifying oligomeric or polymeric units in the





solution state but, for most silver(I) coordination polymers, only dimeric or trimeric species have been observed.⁵⁻⁸ In this work, the technique of cold-spray ionization mass spectrometry (CSI-MS), which is a modified ESI-MS method that is carried out at low temperature,⁸ has been used to probe the structures of silver(I) compounds in solution. The low temperature slows decomposition and so enables observation of higher molecular weight oligomers. The ligands used are the flexible bis(amidopyridine) ligands 1–4 (Scheme 2), and the approach is to crystallize complexes with silver(I), to determine the solid state structures, and then to probe the structures in solution by using the CSI-MS technique. Amides tend to adopt a roughly planar structure, though the barrier to rotation about the RN–CO bond is modest, and N-methylamide

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Scheme 2 The ligands 1–4.

derivatives **1** and **2** are expected to have the methyl group *cis* to oxygen (termed the *cis*-stereochemistry of the MeNCO group), while the simple amide derivatives **3** and **4** are expected to have the *trans*-stereochemistry of the HNCO groups, and may take part in hydrogen bonding.^{46,9} Complexes **1** and **3** have 3-pyridyl substituents while **2** and **4** have 4-pyridyl units, and all ligands are based on a central $1,3-C_6H_4$ unit or its 5-*t*-butyl derivative.

Results

Synthesis and solid state structures of silver(I) complexes

The reaction of $AgBF_4$ with the ligand 1 in a 1 : 1 ratio unexpectedly gave crystals of the complex $[Ag(1)_2][BF_4]$, 5. Complex 5 was then prepared in high yield by carrying out the reaction in a 1 : 2 mole ratio (Scheme 3).



Scheme 3 Reagent: (i) AgBF₄.

The structure of complex 5 is shown in Fig. 1. It is an unusual chelate complex $[Ag(1)_2][BF_4]$ with 14-membered chelate rings. The silver(I) ion has distorted tetrahedral stereochemistry, with



Fig. 1 Structure of the cationic bis(chelate) complex **5**. The tetrafluoroborate anion is not shown. Selected bond parameters: Ag–N(1) 2.316(3); Ag–N(23) 2.312(3) Å; N(1)–Ag–N(1A) 123.7(2); N(23)–Ag–N(23A) 135.0(1); N(1)–Ag–N(23) 104.1(1); N(1)–Ag–N(23A) 96.7(1)°. Torsion angles: C(8)–N(7)–C(9)–O(10) 4.2(6); O(18)–C(17)–N(19)–C(20)–5.3(6)°. Symmetry equivalent: –x, y, $\frac{1}{2}$ – z.

N-Ag-N angles ranging from 96.7(1)-135.0(1)°. The angle associated with the chelate ligand, N(1)-Ag-N(23) = 104.1(1)°, is close to the natural tetrahedral angle. The MeNCO unit of the N-methylamide group has the *cis* geometry as indicated by the torsion angles C(8)-N(7)-C(9)-O(10) = 4.2(6) and O(18)-C(17)- $N(19)-C(20) = -5.3(6)^{\circ}$. However, the aryl and pyridyl groups twist out of this MeNCO plane. Some twist is needed to avoid steric effects with the ortho hydrogen atoms of the aryl groups, but the greater distortion is needed in order to attain the conformation needed for chelation [for example, the plane N(7)C(8)C(9)O(10) is twisted by 65° and 55° with respect to the neighboring aryl and pyridyl groups respectively]. The silver(I) centers lie at a twofold symmetry site, and individual molecules have C_2 symmetry. Complex 5 is the only chelate derivative isolated from the group of ligands 1-4. Evidently any strain arising from the twisting of the aryl groups out of the MeNCO plane of the N-methylamide group is more than compensated for by the chelate effect, with entropy favoring formation of the mononuclear complex.

The reaction of ligand **2** with silver tetrafluoroborate or nitrate gave the macrocyclic complex $[Ag_2(\mu-2)_2(BF_4)][BF_4]$, **6**, or the polymeric complex $[{Ag(\mu-2)(NO_3)}_n]$, **7**, respectively, as shown in Scheme 4. The structure of complex **6** is similar to that reported earlier with the ligand 1,3-C₆H₄[C(=O)NMe-4-C₅H₄N]₂, with one tetrafluoroborate anion loosely bound within the cavity of the macrocycle [Ag \cdots F(52) 2.85(1); Ag(A) \cdots F(51) 2.62(1) Å]. There is an inversion centre in the centre of the macrocycle and so the encapsulated tetrafluoroborate anion is disordered about this position, though only one component is shown for clarity.

Complex 7, whose structure is shown in Fig. 3, exists in the form of a polymeric, sinusoidal chain containing silver(I) cations and bridging bis(pyridine) ligands 2. There are weaker interactions between silver(I) cations and nitrate anions, which are located between pairs of silver(I) cations at distances of Ag...O(42) = 2.76 and Ag(1)...O(42) = 2.68 Å. The angle N(11)-Ag-N(38A) = 165.5(2)^{\circ} is significantly distorted from linearity, presumably as a result of the secondary bonding to the nitrate anions. The MeNCO N-methylamide units of the ligands 2 are in the *cis* geometry, with the torsion angles C(18)-N(17)-C(19)-O(20) = 1.1(5) and O(32)-C(31)-N(33)-C(34) 8.8(6)^{\circ}. The U-shaped structure of each Ag-2-Ag unit (Fig. 3) appears equally well suited to formation of a macrocycle [Ag₂(μ -2)₂]²⁺ as the observed polymer [Ag_n(μ -2)_n]ⁿ⁺. Indeed, the similar ligand



BF₄

Scheme 4 Reagents: (i) AgBF₄; (ii) AgNO₃.

 $NN = 1,3-C_6H_4[C(=O)NMe-4-C_5H_4N]_2$, without the *t*-butyl substituent in **2**, does form the macrocyclic structure $[Ag_2(\mu-NN)_2]^{2+}$ with an encapsulated nitrate anion,⁶ and it is clear that the ligand **2** adopts similar conformations in both the macrocyclic and polymeric structures.



Fig. 2 Structure of the macrocyclic complex **6**. Selected bond parameters: Ag–N(11) 2.15(1); Ag–N(38A) 2.15(1) Å; N(11)–Ag–N(38A) 177.4(4)°. Symmetry equivalent: 1–x, 1–y, –z.

The ligand **3** gave crystalline silver(1) complexes on reaction with silver trifluoroacetate or silver nitrate, which were shown to have the polymeric structure $[{Ag(\mu-3)}_n](CF_3CO_2)_n$, **8**, or macrocyclic structure $[Ag_2(\mu-3)_2](NO_3)_2$, **9**, respectively, according



Fig. 3 Structure of the polymeric complex 7. Selected bond parameters: Ag–N(11) 2.191(3); Ag–N(38A) 2.187(4) Å; N(11)–Ag–N(38A) 165.5(2)°. Torsion angles: C(18)–N(17)–C(19)–O(20) –1.1(5); O(32)–C(31)–N(33)–C(34) 8.8(6)°. Symmetry equivalents: A, $\frac{1}{2}$ – x, $\frac{1}{2}$ + y, 2 – z; B, $\frac{1}{2}$ – x, $-\frac{1}{2}$ + y, 2 – z.

to Scheme 5. The polymeric and macrocyclic complexes require different conformations of the ligand 3, illustrated as 3a and 3b in Scheme 5. Thus, the ligands 2 and 3 have each yielded both macrocyclic and polymeric forms of their silver(I) complexes.



Scheme 5 Reagents: (i) AgO₂CCF₃; (ii) AgNO₃.

The structure of polymer **8** is shown in Fig. 4. Fig. 4(a) shows part of a single polymer chain and illustrates how both trifluoroacetate anions form very weak secondary bonds to Ag(1) $[Ag(1) \cdots O(32) = 3.13 \text{ Å}]$ while also being "chelated" by hydrogen bonding to the two NH groups of the ligand in conformation **3a** $[N(8) \cdots O(31) \ 3.173(5); N(19) \cdots O(31) \ 2.993(6) \text{ Å}]$. Both silver atoms are at centres of symmetry so the NAgN and OAgO angles are strictly linear. Fig. 4(b) shows sections of three neighboring polymer chains. The polymers are connected by three types of secondary bonds to form a sheet structure.



Fig. 4 Views of the structure of complex **8**: (a) part of a polymer chain, showing the interactions of the trifluoroacetate anions with NH groups and with Ag(1); (b) part of a supramolecular sheet, showing secondary bonding to Ag(2B) and π -stacking of phthalamide groups. Selected bond parameters: Ag(1)–N(1) 2.108(5); Ag(2)–N(23) 2.154(4) Å; N(1A)–Ag(1)–N(1) = N(23A)–Ag(2)–N(23) = 180°. Hydrogen bond distances: N(8) \cdots O(31) 3.173(5); N(19) \cdots O(31) 2.993(6) Å. Symmetry equivalent: A, –x–1, –y–2; –z.

Firstly, the trifluoroacetate anions serve to link chains through forming bridging $(NH)_2 \cdots OCO \cdots Ag(1)$ units, as described above. Secondly, the Ag(2) atoms are linked through secondary bonding to carbonyl groups of neighboring chains to form C=O(10) \cdots Ag(2) \cdots O(10)=C units with Ag(2) \cdots O(10) = 2.82 Å]. Thirdly, pairs of phthalamide groups from neighboring chains are parallel to each other, separated by 3.3 Å and form a π -stacking interaction. The phthalamide groups are twisted with respect to the chain direction to allow this π -stacking and so the chains are tightly intermeshed, with the helicity alternating between *P* and *M* and with the π -stacking between *PM* pairs (Fig. 4b).

The large macrocyclic structure of complex **9** [Ag \cdots Ag(B) = 10.08 Å] is shown in Fig. 5, which shows that the ligands are in conformation **3b**. There is an inversion centre at the centre of each macrocycle, so all silver atoms are equivalent. Each macrocycle is associated with the neighbouring macrocycle through silver \cdots silver interactions [Ag \cdots Ag(1) = 3.3629(8) Å], supported by secondary bonding to the nitrate anions [Ag(1) \cdots O(41) = 2.85, Ag \cdots O(41) = 2.62 and Ag \cdots O(42) = 2.91 Å] to give a chain of metallocycles.

The dimensionality of the supramolecular structure is further increased because each macrocycle is hydrogen bonded intermolecularly to four other macrocycles by hydrogen bonding between the amide groups of the type $NH \cdots O=C[N(29) \cdots O(28) = 2.866(4); N(18) \cdots O(20) = 2.842(4) Å]$ as shown in Fig. 6. The hydrogen bonding links a given macrocycle to two macrocycles in each of the polymer chains on either side to give a supramolecular sheet of macrocycles (Fig. 6).

The reaction of ligand 4 with silver trifluoroacetate gave the polymeric complex 10, as shown in Scheme 6.



Fig. 5 The structure of complex 9, showing two macrocycles connected through secondary Ag···Ag and Ag···O bonds. Selected bond parameters: Ag–N(11) 2.158(4); Ag–N(33) 2.147(4); Ag···Ag(1) 3.3629(8) Å; N(33)–Ag–N(11) 167.1(1)°. Symmetry equivalents: A, 2–x, –y, 1–z; B, 1–x, –y, 1–z.



Fig. 6 A view of part of the supramolecular sheet structure of complex 9, showing both the Ag \cdots Ag and NH \cdots O=C bonding interactions. The nitrate groups are omitted for clarity. Hydrogen bond distances: N(18) \cdots O(20) 2.842(4); N(29) \cdots O(28) 2.866(4) Å.

The asymmetric unit in the structure of complex 10 is shown in Fig. 7. It illustrates the conformation of the phthalamide unit which allows "chelation" of the trifluoroacetate anion by the two NH hydrogen bond donors $[N(8) \cdots O(32A) 2.943(3);$ $N(19) \cdots O(32A) 3.012(4)$ Å]. Propagation of this structure gives rise to a coordination polymer.

The polymers and the association between polymer chains in complex 10 are shown in Fig. 8. Within each polymer chain, the helicity of the ligands 4 are all the same (P or M). The chains are crosslinked through complementary C=O...Ag bonding and there are two types of association. The stronger association is



Scheme 6 Reagent: (i) AgO₂CCF₃.



Fig. 7 The asymmetric unit in the structure of complex 10, showing the "chelation" of the trifluoroacetate anion by two NH hydrogen bond donors. Selected bond parameters: Ag–N(1) 2.177(3); Ag–N(24) 2.167(2), N(1)–Ag–N(24A) 170.6(1). Hydrogen bond distances: N(8)···O(32A) 2.943(3); N(19)···O(32A) 3.012(4) Å.

between units such as Ag \cdots O(10D) = 2.563(2) Å in neighboring chains, shown in red in Fig. 8, and this gives rise to a double stranded polymer. These pairs of polymer chains have opposite helicity, and are related by inversion symmetry. The double stranded polymers are connected to polymers on each side (shown in blue in Fig. 8) by weaker intermolecular interactions such as Ag \cdots O(18A) = 2.630(2) Å. The overall result is to form a supramolecular "sheet of polymers" structure in which the polymer chains have alternating *PMPM* helicity (Fig. 8).



Fig. 8 The supramolecular "sheet of polymers" structure of complex 10, with anions and *t*-butyl groups omitted for clarity. The stronger association is between polymers shown in red: $Ag \cdots O(10D) 2.563$ (2); $Ag \cdots O(18A) = 2.630(2)$ Å; N(1)–Ag–O(10) 88.4(1); N(24)–Ag– $O(10) 99.40(9)^\circ$. Symmetry equivalents: A, –x, 1–y, –2–z; B, 1+x, –1+y, 1+z; C, 1–x, 1–y, –2–z.

CSI-MS studies of complexes in solution

NMR studies of these complexes in solution were of limited value because dynamic exchange occurred, so the degree of aggregation was probed by using positive ion CSI-MS. The experiments were carried out using solutions in acetonitrile at temperatures ranging from 0 to -30 °C, and masses are given for the ¹⁰⁷Ag isotopomers. It should be noted that the solvents used for the syntheses, NMR and CSI-MS are typically different. Thus, for example, the crystals were usually grown from mixed solvents and could not be grown from acetonitrile, while the mixed solvent systems are unsuited to the NMR experiments and also, to a lesser extent, the CSI-MS experiments. We have recorded both NMR and CSI-MS experiments of complexes 8-10 in acetonitrile and in dichloromethane-methanol, and shown that they are very similar (Experimental section), but the quantitative aspects of the equilibria are certainly expected to be solvent as well as anion dependent.3 All complexes gave good CSI-MS data from CH₃CN solution and these are described below.

The CSI-MS of the complex $[Ag(1)_2][BF_4]$, 5, gave envelopes of peaks at m/z = 799, 494, 453 and 347, assigned to $[Ag(1)_2]^+$, [Ag(1)(MeCN)]⁺, [Ag(1)]⁺, and [(1)H]⁺, respectively. There were no significant ions containing more than a single silver atom, indicating that the chelate structure is maintained in solution, albeit with some solvolysis. In contrast, the macrocyclic complex $[Ag_{2}(2)_{2}(BF_{4})][BF_{4}], 6$, gave envelopes of peaks at m/z = 1105, 550, and 403, assigned to [Ag₂(2)₂(BF₄)]⁺, [Ag(2)(MeCN)]⁺ and [(2)H]⁺, respectively, indicating that the macrocyclic structure was largely maintained in solution. The polymeric complex $[{Ag(2)}_n](NO_3)_n$, 7, gave envelopes of peaks at m/z = 2053, 1809, 1482, 1080, 911, 550, and 403, assigned to $[Ag_3(2)_4(NO_3)]^+$, $[Ag_2(2)_3(NO_3)]^+$, $[Ag_2(2)_2(NO_3)]^+$, $[Ag(2)_2]^+$, $[Ag(2)(MeCN)]^+$ and $[(2)H]^+$, respectively. Some of these peaks are equivalent to those for complex 6, probably indicating the presence of some macrocyclic complex $[Ag_2(\mu-2)_2(NO_3)]^+$ in solution. However, the observation of peaks for $[Ag_3(2)_4(NO_3)]^+$ and $[Ag_2(2)_3(NO_3)]^+$ indicates that there are also ring-opened oligomers present.

The CSI-MS of the polymeric complex $[{Ag(3)}_n](CF_3CO_2)_n, 8$, revealed envelopes of peaks centered at $m/z = 2025 [Ag_5(3)_3X_4]^+$, 1805 $[Ag_4(3)_3X_3]^+$, 1459 $[Ag_4(3)_2X_3]^+$, 1239 $[Ag_3(3)_2X_2]^+$, 1019 $[Ag_2(3)_2X]^+$, 799 $[Ag(3)_2]^+$, 453 $[Ag(3)]^+$ and 347 $[(3)H]^+$, with X = CF_3CO_2. For comparison, the macrocyclic complex $[Ag_2(3)_2](NO_3)_2$, 9, gave envelopes of peaks at m/z =2167 $[Ag_5(3)_4X_4]^+$, 1998 $[Ag_4(3)_4X_3]^+$, 1652 $[Ag_4(3)_3X_3]^+$, 1483 $[Ag_3(3)_3X_2]^+$, 968 $[Ag_2(3)_2X]^+$, 799 $[Ag(3)_2]^+$, 453 $[Ag(3)]^+$ and 347 $[(3)H]^+$, with X = NO_3. In this case, there are many similarities, suggesting that both exist in solution as a mixture of macrocyclic and ring-opened oligomeric forms.

The CSI-MS of the polymeric complex $[{Ag(4)}_n](CF_3CO_2)_n$, **10**, in acetonitrile showed envelopes of peaks centered at m/z =1753 $[Ag_3(4)_3X_2]^+$, 1533 $[Ag_2(4)_3X]^+$, 1355 $[Ag_3(4)_2X_2]^+$, 1313 $[Ag(4)_3]^+$, 1131 $[Ag_2(4)_2X]^+$, 911 $[Ag(4)_2]^+$, 731 $[Ag_2(4)X]^+$, 550 $[Ag(4)(MeCN)]^+$, 509 $[Ag(4)]^+$ and 403 $[(4)H]^+$. The peak at m/z =1313, corresponding to $[Ag(4)_3]^+$, indicates the presence of some three coordinate silver(1) ions in solution.

Discussion

Based on the structures of the crystalline complexes and on the CSI-MS data, it can be argued that the ring-opening

polymerization involves some of the compounds in Scheme 7. When chelation to give complexes of type C (complex 5, Fig. 1) cannot occur, the complexes tend to crystallize as either the macrocycles of type D (complexes 6, Fig. 2; 9, Fig. 5) or the polymers of type \mathbf{K} , n = infinity (complexes 7, Fig. 3; 8, Fig. 4; 10, Fig. 8). It is unusual, in studies of this kind, to be able to isolate larger macrocycles such as E or ring-opened oligomers such as G-K in Scheme 7.^{4,10} In the CSI-MS, only singly charged cations have been observed, indicating tight ion-pairing with anions, probably through either $Ag^+ \cdots X^-$ or $NH \cdots X^-$ interactions. Only the covalently linked anions are shown in Scheme 7, and the likely folding of the oligomers arising from secondary bonding interactions (see Fig. 3 for example) is ignored. As well as the compounds in Scheme 7 that are proposed to be involved in forming the polymers, the CSI-MS indicates the presence of ions of general formula [Ag(NN)(MeCN)]⁺ and (Ag(NN)₃]⁺, indicating more extensive ligand exchange with involvement of solvent acetonitrile molecules or silver(I) compounds with higher coordination number. The dynamic ligand exchange is likely to occur by an associative mechanism, involving reversible exchange between pyridyl, anion and solvent molecules. The end groups in the ring opened oligomers can be κ^1 -bipyridine (F, G, K), anion X^{-} (I), or one of each group (J). By adding the number of anions needed to give singly charged cations, these ions, as observed in the CSI-MS, will have formulae $[Ag_n(NN)_{n+1}X_{n-1}]^+$, $[Ag_n(NN)_{n-1}X_{n-1}]^+$, and $[Ag_n(NN)_nX_{n-1}]^+$, respectively. The results of the CSI-MS experiments are consistent with this picture, with the exception of the observed ion $[Ag_5(3)_3X_4]^+$, $X^- =$ trifluoroacetate, in the CSI-MS of complex 8. One possibility is that this ion may involve association between a dimer [Ag₂(O₂CCF₃)₂]¹¹ and an oligomer $[Ag_3(3)_3(O_2CCF_3)_2]^+$, but the CSI-MS only gives the overall formula. It should also be noted that the formula $[Ag_n(NN)_nX_{n-1}]^+$ is consistent with either the oligomeric ring-opened structure (J) or the macrocyclic structure (D, E).

This work has shown the fine balance between formation of macrocyclic and polymeric complexes which can be switched by minor changes in the bipyridine ligand structure. The higher order structures are dependent on hydrogen bonding, when possible, or on secondary bonding effects which may include both $Ag \cdots X$ and $Ag \cdots Ag$ bonding. The combination of crystallography and CSI-MS gives an insight into how the complex structures are built up from the simple building blocks.

Experimental

¹H and ¹³C{¹H} spectra were recorded using a Varian Mercury 400 spectrometer. The labeling scheme for the NMR spectra is described in Scheme 8. CSI mass spectra were recorded using a modified Micromass LCT spectrometer at a desolvation temperature of -10 to -30 °C and were calibrated with CsI at a concentration of 10µg µl⁻¹ in acetonitrile. Solvents were dried immediately before use in reactions with water sensitive reagents.



Scheme 8 Proton labeling scheme for ligands 1–4.

5-tert-Butyl-C₆H₃-1,3-[C(=O)NMe-4-C₅H₄N]₂, 2

To a solution of 4-(aminomethyl)pyridine (1.0 g, 9.2 mmol) and excess Et₃N (1.4 mL, 13.9 mmol) in CH₂Cl₂ (50 mL), was added a solution of 5-*tert*-butylisophthaloyl chloride (1.2 g, 4.6 mmol) in CH₂Cl₂ (10 mL). The reaction mixture was stirred at room temperature under nitrogen for 12 h, the solvent was evaporated under vacuum, the product was extracted with benzene, and the solvent was evaporated to give the product as a white solid. Yield: 1.56 g (98%). NMR in CDCl₃: δ (¹H) = 8.43 [d, 4H, *J*(HH) = 5 Hz, H2']; 7.83 [t, 1H, *J*(HH) = 5 Hz, H2']; 7.13 [d, 2H, *J*(HH) = 2 Hz, H4]; 6.82 [d, 4H, *J*(HH) = 5 Hz, H3']; 3.46 [s, 6H, CH₃]; 0.91 [s, 9H, t-Bu]. δ (¹³C) = 169.8 (C=O), 151.9, 150.9, 150.6, 150.5, 134.9, 122.0, 126.6, 120.5, 37.3 (CH₃), 30.5 (*t*-Bu). Anal. Calcd. for C₂₄H₂₆N₄O₂: C, 71.62; H, 6.51; N, 13.92. Found: C, 71.14; H, 6.85; N, 13.70%.

$1,3-C_6H_4[C(=O)NH-CH_2-3-C_5H_4N]_2, 3$

To a solution of a mixture of 3-(aminomethyl)pyridine (3.0 g, 14.8 mmol) and excess triethylamine (6.2 mL, 44.3 mmol) in



Scheme 7 Some of the likely cations involved in the ring-opening polymerization.

CH₂Cl₂ (80 mL), was added a solution of isophthaloyl chloride (3.2 g; 29.6 mmol) in CH₂Cl₂ (20 mL). The reaction mixture was stirred at room temperature under nitrogen overnight. The solvent was evaporated under vacuum and the yellow residue was redissolved in thf (20 mL) and filtered. The solvent was evaporated under vacuum to give the product as a white solid. Yield: 3.72 g (73%). NMR in CD₂Cl₂/dmf- d_7 : $\delta(^1\text{H}) = 8.58$ [t, 2H, J(HH) = 6 Hz, CONH]; 8.48 [s, 2H, H2']; 8.39 [d, 2H, J(HH) = 6 Hz, H6']; 8.25 [t, 1H, J(HH) = 2 Hz, H2]; 7.96 [d, 2H, J(HH) = 8 Hz, H4']; 7.75 [dt, 2H, J(HH) = 8 Hz, 2 Hz, H4]; 7.48 [t, 1H, J(HH) =8 Hz, H5]; 7.29 [dd, 2H, J(HH) = 6 Hz, 8 Hz, H5']; 4.57 [d, 4H, J(HH) = 6 Hz, CH₂]; NMR in (CD₃)₂SO: $\delta(^{1}H) = 9.26$ [t, 2H, J(HH) = 6 Hz, CONH]; 8.57 [d, 2H, J(HH) = 2 Hz, H2']; 8.46 [dd, 2H, J(HH) = 5 Hz, 2 Hz, H6']; 8.38 [s, 1H, H2]; 8.02 [dd, 2H, HJ(HH) = 8 Hz, 2 Hz, H4']; 7.75 [d, 2H, J(HH) = 8 Hz, H4]; 7.58 [t, 1H, *J*(HH) = 8 Hz, H5]; 7.37 [dd, 2H, *J*(HH) = 5 Hz, 8 Hz, H5']; 4.51 [d, 4H, J(HH) = 6 Hz, CH_2]. NMR in CD_2Cl_2/CD_3OD : $\delta(^{13}C) = 168.1 \ (C=O), \ 149.0, \ 148.3, \ 136.9, \ 135.5, \ 134.9, \ 131.0, \ 148.3, \ 136.9, \ 135.5, \ 134.9, \ 131.0, \ 148.3, \ 136.9, \ 135.5, \ 134.9, \ 131.0, \ 148.3, \ 136.9, \ 135.5, \ 134.9, \ 131.0, \ 148.3, \ 136.9, \ 135.5, \ 134.9, \ 131.0, \ 148.3, \ 136.9, \ 135.5, \ 134.9, \ 131.0, \ 148.3, \ 136.9, \ 135.5, \ 134.9, \ 131.0, \ 148.3, \ 136.9, \ 135.5, \ 134.9, \ 131.0, \ 148.3, \ 136.9, \ 135.5, \ 134.9, \ 131.0, \ 148.3, \ 136.9, \ 135.5, \ 134.9, \ 131.0, \ 148.3, \ 136.9, \ 135.5, \ 134.9, \ 131.0, \ 148.3, \ 136.9, \ 135.5, \ 134.9, \ 131.0, \ 148.3, \ 136.9, \ 135.5, \ 134.9, \ 136.9, \$ 129.4, 126.31, 124.43, 41.9 (CH2). Anal. Calcd for C20H18N4O2: C: 69.35; H: 5.24; N: 16.17. Found: C: 69.13; H: 5.36; N: 15.90%.

5-tert-Butyl-1,3-C₆H₃[C(=O)NH-CH₂-4-C₅H₄N]₂, 4

To a solution of a mixture of 4-(aminomethyl)pyridine (0.4 g, 7.7 mmol) and excess triethylamine (1.61 mL, 11.5 mmol) in thf (50 mL), was added a solution of 5-*tert*-butyl-isophthaloyl chloride (1 g, 3.8 mmol) in thf (10 mL). The reaction mixture was stirred at room temperature under nitrogen overnight. The resulting mixture was filtered to obtain the yellow product. The product was washed twice with water (30 mL) and a small amount of thf, and then dried under vacuum overnight. Yield: 1.31 g (85%). NMR in CD₂Cl₂/CD₃OD: δ (¹H) = 8.40 [br d, 4H, *J*(HH) = 5 Hz, H2'], 8.12 [t, 1H, *J*(HH) = 2 Hz, H2]; 8.07 [d, 2H, *J*(HH) = 2 Hz, H4]; 7.26 [dd, 4H, *J*(HH) = 5 Hz, 2 Hz, H3']; 4.58 [d, 4H, *J*(HH) = 6 Hz, CH₂]; 1.33 [s, 9H, t-Bu]. δ (¹³C) = 168.6 (C=O), 153.1, 149.6, 149.4, 134.6, 128.4, 123.6, 123.1, 68.4 (CH₂), 31.1 (CH₃). Anal. Calcd for C₂₄H₂₆N₄O₂: C: 71.62; H: 6.51; N: 13.92%. Found: C: 71.56; H: 6.87; N: 13.74%.

[Ag(1)₂][BF₄], 5

To a solution of AgBF₄ (0.040 g, 0.205 mmol) in thf (10 mL) was added a solution of ligand **1** (0.142 g, 0.41 mmol) in CH₂Cl₂ (10 mL). The mixture was stirred for 4 h, then pentane (20 mL) was added to precipitate the product as a white solid, which was collected by filtration, washed with ether and dried under vacuum. Yield: 0.108 g (59%). NMR in dmf- d_7 : δ (¹H) = 8.43 [d, 2H, *J*(HH) = 5 Hz, H6']; 8.30 [m, 2H, H2']; 7.72 [dd, 2H, *J*(HH) = 8 Hz, 5 Hz, H5']; 7.64 [m, 2H, H5]; 7.01 [m, 4H, *J*(HH) = 8 Hz, H4, H6, H4']; 3.52 [2, 6H, MeN]. Anal. Calcd for C₄₀H₃₆AgBF₄N₈O₄: C, 54.14; H, 4.09; N, 12.63. Found: C, 53.68; H, 3.87; N, 12.24%. Colourless crystals of **5** were obtained by slow diffusion of solutions of [AgBF₄] in thf and ligand **1** in CH₂Cl₂.

$[Ag_2(\mu-2)_2][BF_4]_2, 6$

To a solution of $[AgBF_4]$ (0.04 g, 0.206 mmol) in thf (10 mL) was added a solution of ligand **2** (0.083 g, 0.206 mmol) in CH₂Cl₂ (10 mL). The mixture was stirred for 4 h, then pentane (20 mL)

was added to precipitate the product as a white solid, which was collected by filtration, washed with ether and dried under vacuum. Yield: 0.104 g (84%). NMR in CDCl₃/CD₃OD: $\delta(^{1}H) = 8.47$ [d, 4H, J(HH) = 6 Hz, H2']; 7.43 [s, 1H, H2]; 7.34 [s, 2H, H4]; 7.05 [d, 4H, J(HH) = 5 Hz, H3']; 3.51 [s, 6H, MeN]; 1.02 [s, 9H, t-Bu]. Anal. Calcd. for C₂₄H₂₆AgBF₄N₄O₂: C, 48.27; H, 4.39; N, 9.38. Found: C, 48.65; H, 4.28; N, 9.74%. Colourless plates of **6**·4CH₂Cl₂ were grown by slow diffusion of solutions of AgBF₄ in thf and ligand **2** in CH₂Cl₂.

$[{Ag(\mu-2)}_n][NO_3]_n, 7$

To $[AgNO_3]$ (0.04 g, 0.236 mmol) in thf/water (10 mL/2 mL) was added a solution of ligand **2** (0.095 g, 0.236 mmol) in a mixture of CH₂Cl₂ (10 mL) and methanol (2 mL). The mixture was stirred for 4 h, then pentane (20 mL) was added to precipitate the product as a white solid, which was collected by filtration, washed with acetone and dried under vacuum. Yield: 0.089 g (69%). NMR in CDCl₃/CD₃OD: δ ('H) = 8.33 [d, 4H, *J*(HH) = 6 Hz, H2']; 7.67 [d, 2H, *J*(HH) = 1 Hz, H4]; 6.78 [s, 1H, H2]; 6.72 [d, 4H, *J*(HH) = 6 Hz, H3']; 3.32 [s, 6H, MeN]; 1.22 [s, 9H, *t*-Bu]. Anal. Calcd. for C₂₄H₂₆AgN₅O₅: C, 50.36; H, 4.58; N: 12.24%. Found: C, 49.96; H, 4.23; N, 12.21%. Colourless plates of **7** were grown by slow diffusion of solutions of AgNO₃ in aqueous thf and ligand **2** in CH₂Cl₂.

$[{Ag(\mu-3)}_n][CF_3CO_2]_n, 8$

To a solution of [AgO₂CCF₃] (0.030 g, 0.136 mmol) in acetone (10 mL) was added a solution of ligand 3 (0.047 g, 0.136 mmol) in a mixture of CH₂Cl₂ (10 mL) and methanol (2 mL). The mixture was stirred for 4 h, then pentane (20 mL) was added to precipitate the product as a white solid, which was collected by filtration, washed with acetone and dried under vacuum. Yield: 0.050 g (65%). NMR in CD₂Cl₂/dmf- d_7 : $\delta(^1\text{H}) = 9.10$ [t, 2H, J(HH) = 6 Hz, CONH]; 8.71 [br s, 2H, H2']; 8.53 [br s, 1H, H2]; 8.47 [d, 2H, J(HH) = 5 Hz, H6']; 8.02 [d, 2H, J(HH) = 8 Hz, H4']; 7.84 [d, 2H, J(HH) = 8 Hz, H4]; 7.47 [t, 1H, J(HH) = 8 Hz, H5];7.35 [dd, 2H, J(HH) = 8 Hz, 5 Hz, H5']; 4.60 [d, 4H, J(HH) = 6 Hz, CH₂]. NMR in CD₃CN: $\delta(^{1}H) = 9.26$ [t, 2H, J(HH) = 6 Hz, CONH]; 8.75 [br s, 2H, H2']; 8.47 [br s, 1H, H2]; 8.32 [d, 2H, J(HH) = 5 Hz, H6'; 7.98 [d, 2H, J(HH) = 8 Hz, H4']; 7.76 [d, 2H, J(HH) = 8 Hz, H4]; 7.47 [t, 1H, J(HH) = 8 Hz, H5]; 7.31 [dd, 2H, J(HH) = 8 Hz, 5 Hz, H5']; 4.54 [d, 4H, J(HH) = 6 Hz, CH₂]. CSI-MS in CH₂Cl₂-MeOH: $m/z = 2025 [Ag_5(3)_3(CF_3CO_2)_4]^+$, 1805 $[Ag_4(3)_3(CF_3CO_2)_3]^+$, 1459 $[Ag_4(3)_2(CF_3CO_2)_3]^+$, 1239 $[Ag_3(3)_2(CF_3CO_2)_2]^+$, 1019 $[Ag_2(3)_2(CF_3CO_2)]^+$. Anal. Calcd. for C₂₂H₁₈AgF₃N₄O₄: C, 46.58; H, 3.20; N, 9.88. Found: C, 46.11; H, 2.82; N, 9.45%. Colourless crystals of 8 were obtained by slow diffusion of an equal equivalent of [AgO₂CCF₃] in acetone into a concentrated solution of ligand 3 in a mixture of CH₂Cl₂ and methanol.

$[{Ag(\mu-3)}_n][NO_3]_n, 9$

This was prepared in a similar way as for complex **8** except that AgNO₃ was used. Yield: 91%. NMR in dmso- d_6 : $\delta({}^{1}\text{H}) = 9.25$ [t, 2H, J(HH) = 5 Hz, CONH]; 8.56 [br s, 2H, H2']; 8.48 [d, 2H, J(HH) = 5 Hz, H6']; 8.37 [s, 1H, H2]; 8.02 [d, 2H, J(HH) = 8 Hz, H4']; 7.79 [d, 2H, J(HH) = 8 Hz, H4]; 7.58 [t, 1H, J(HH) = 8 Hz,

Complex	5	$6.4CH_2Cl_2$	7	8	9	$10{\cdot}CH_2Cl_2{\cdot}solvent$
Formula	$C_{40}H_{36}AgBF_4N_8O_4$	$C_{52}H_{60}Ag_{2}B_{2}Cl_{8}F_{8}N_{8}O_{4} \\$	$C_{24}H_{26}AgN_5O_5$	$C_{22}H_{18}AgF_3N_4O_4$	$C_{20}H_{18}AgN_5O_5$	$C_{27}H_{28}AgCl_2F_3N_4O_4$
FW	887.45	1534.04	572.37	567.27	516.26	708.30
$T(\mathbf{K})$	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Cryst. syst.	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space gp.	C2/c	<i>P</i> 2/ <i>c</i>	<i>C</i> 2	$P2_{1}/c$	Pbca	$P\overline{1}$
a (Å)	22.440(1)	16.034(1)	16.4077(6)	10.7454(3)	13.2247(5)	10.7192(4)
$b(\mathbf{A})$	15.230(1)	10.4349(6)	9.8095(4)	11.3948(4)	9.6779(3)	12.2831(7)
c (Å)	15.933(1)	20.490(1)	14.9862(5)	18.2357(8)	30.769(1)	13.4164(7)
$\alpha(\circ)$	90	90	90	90	90	67.884(2)
$\beta(\circ)$	134.747(3)	105.409(3)	93.438(2)	99.076(2)	90	77.113(3)
γ (°)	90	90	90	90	90	74.065(3)
$V(Å^3)$	3867.4(5)	3305.1(4)	2407.7(1)	2204.8(1)	3938.0(2)	1559.3(1)
Z	4	2	4	4	8	2
$d_{\rm c} ({\rm Mg}{\rm m}^{-3})$	1.524	1.541	1.579	1.709	1.742	1.509
Abs. coeff. (mm ⁻¹)	0.524	0.986	0.883	0.977	1.069	0.873
Data/restr./param.	3408/3/276	5670/14/449	4226/1/317	3888/0/310	3495/0/280	5443/4/415
Goof	1.087	1.041	1.041	1.051	1.015	1.123
$R_1, I > 2\sigma(I)$	0.043	0.108	0.035	0.055	0.044	0.038
wR_2 , all data	0.105	0.367	0.078	0.107	0.125	0.094

 Table 1
 X-ray data for the complexes

H5]; 7.42 [dd, 2H, J(HH) = 5 Hz, 8 Hz, H5']; 4.51 [d, 4H, J(HH) = 6 Hz, CH₂]. NMR in CD₃CN: $\delta(^{1}H) = 9.19$ [t, 2H, J(HH) = 5 Hz, CONH]; 8.55 [br s, 2H, H2']; 8.43 [d, 2H, J(HH) =5 Hz, H6']; 8.31 [s, 1H, H2]; 7.99 [d, 2H, J(HH) = 8 Hz, H4']; 7.78 [d, 2H, J(HH) = 8 Hz, H4]; 7.51 [t, 1H, J(HH) = 8 Hz, H5]; 7.40 [dd, 2H, J(HH) = 5 Hz, 8 Hz, H5']; 4.48 [d, 4H, J(HH) = 6 Hz, CH₂]. CSI-MS in CH₂Cl₂–MeOH: m/z = 2167[Ag₅(3)₄(NO₃)₄]⁺, 1998 [Ag₄(3)₄(NO₃)₃]⁺, 1652 [Ag₄(3)₃(NO₃)₃]⁺, 1483 [Ag₃(3)₃(NO₃)₂]⁺, 968 [Ag₂(3)₂(NO₃)]⁺, 799 [Ag(3)₂]⁺. Anal. Calcd for C₂₀H₁₈AgN₅O₅: C, 46.53; H, 3.51; N, 13.57. Found: C, 46.07; H, 3.32; N, 13.26%. Colourless needles of **9** were obtained by slow diffusion of solutions of AgNO₃ in aqueous acetone and ligand **3** in a mixture of CH₂Cl₂ and methanol.

${[Ag(\mu-4)][CF_3CO_2]}_n, 10$

This was prepared in a similar way as for complex **8** except that ligand **4** was used. Yield: 92%. NMR in CD₃OD: $\delta(^{1}H) = 8.56$ [d, 4H, *J*(HH) = 5 Hz, H2']; 8.27 [t, 1H, *J*(HH) = 2 Hz, H2]; 8.15 (d, 2H, *J*(HH) = 2 Hz, H4]; 7.54 [d, 4H, *J*(HH) = 5 Hz, H3']; 4.68 [d, 4H, CH₂]; 1.40 [s, 9H, t-Bu]. NMR in CD₃CN: $\delta(^{1}H) = 8.53$ [d, 4H, *J*(HH) = 5 Hz, H2']; 8.30 [t, 1H, *J*(HH) = 2 Hz, H2]; 8.11 (d, 2H, *J*(HH) = 2 Hz, H4]; 7.55 [d, 4H, *J*(HH) = 5 Hz, H3']; 4.65 [d, 4H, CH₂]; 1.34 [s, 9H, t-Bu]. CSI-MS in CH₂Cl₂–MeOH: *m*/*z* = 1753 [Ag₃(4)₃(CF₃CO₂)₂]⁺, 1533 [Ag₂(4)₃(CF₃CO₂)]⁺, 1355 [Ag₃(4)₂(CF₃CO₂)]⁺, 1131 [Ag₂(4)₂(CF₃CO₂)]⁺, 911 [Ag(4)₂]⁺, 731 [Ag₂(4)(CF₃CO₂)]⁺. Anal. Calcd. for C₂₆H₂₆AgF₃N₄O₄: C, 50.10; H, 4.20; N, 8.99. Found: C, 49.84; H, 4.51; N, 8.86%. Colourless plates of **10**·CH₂Cl₂ were obtained by slow diffusion of solutions of AgO₂CCF₃ in aqueous acetone and ligand **4** in CH₂Cl₂-methanol.

X-ray structure determination

Crystals were mounted on glass fibers, and data were collected using a Nonius Kappa-CCD diffractometer with COLLECT (Nonius, 1998) software. The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using the Nonius DENZO package. The data were scaled using SCALEPACK (Nonius, 1998). The SHELXTL-NT V6.1 (Sheldrick, G. M., Madison, WI) program package was used to solve and refine the structure by direct methods. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon atoms. Details of the data collection and refinement are given in Table 1. Unusual features are discussed briefly below:

$[Ag_{2}(\mu \text{--}2)_{2}][BF_{4}]_{2}\text{-}4CH_{2}Cl_{2}, 6$

The B–F bond lengths of BF_4^- groups and the C–Cl distances of solvent molecules were fixed at 1.388 Å and 1.65 Å, respectively. One solvent molecule was modeled as a 50:50 disorder. The parameters are imprecise because of solvent disorder, but the connectivity is well-established.

$[Ag(\mu-4)][CF_3CO_2] \cdot CH_2Cl_2, 10$

The *tert*-butyl groups were disordered and were modeled at a 60/40 ratio. The solvent was modeled at a 45/55 ratio of two orientations with the C–Cl bonds fixed at 1.72 Å. There was some unaccounted for electron density which could not be successfully modeled. It was attributed to disordered solvent, and was removed by using SQUEEZE.¹²

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