Ring-opening polymerisation of coordination compounds: a silver(I) network with both ring and polymer components

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Received (in Cambridge, UK) 15th July 2005, Accepted 5th August 2005
First published as an Advance Article on the web 31st August 2005
DOI: 10.1039/b510080a

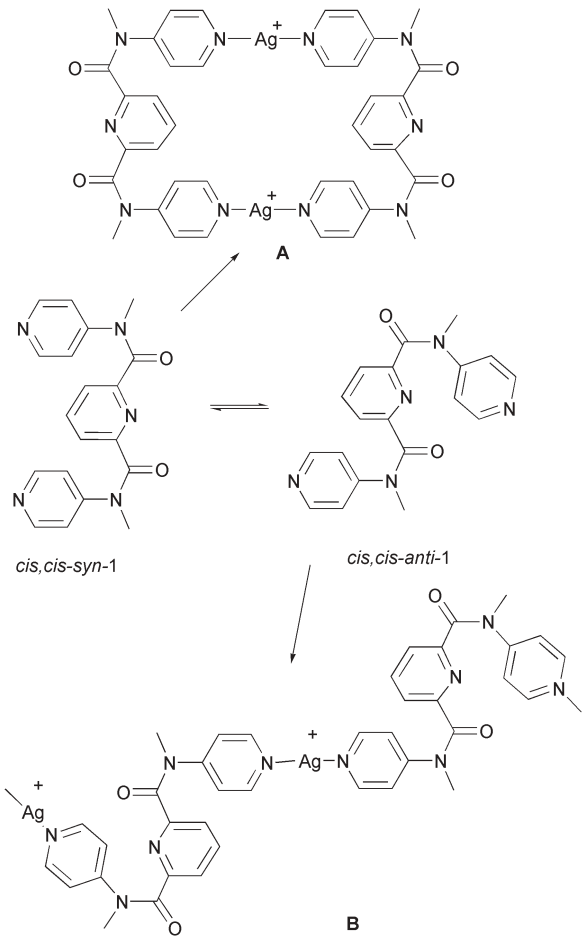
The terpyridyl ligand 2,6-$C_5H_3N\{C(=O)N(Me)$-4-$C_5H_4N\}_2$, 1, combined with silver(I) salts to give the complexes $[Ag_2(1)_2][BF_4]_2$, 2, and $[\{Ag_3(1)_2\}_n][CF_3SO_3]_{3n}$, 3; the network structure of complex 3 contains both macrocyclic units $[Ag_2(\mu\text{-}1)_2]^{2+}$ and ring-opened polymeric units $[\{Ag(\mu\text{-}1)\}_n]^{n+}$.

There is intense current interest in ring-opening polymerization (ROP) of macrocyclic transition metal complexes to give polymers with metals in the backbone structure.[1] Several cases are known in which easy, reversible ring-opening of macrocyclic complexes containing labile transition metal centres can occur in solution, and crystallization can then yield either the ring or polymer form.[1,2] The preferred form may be determined by template effects involving guest or solvent molecules, or by secondary bonding involving counterions, and the polymers may exist in isomeric forms called supramolecular isomers.[1–3] However, there are remarkably few cases in which *both* ring and polymer forms are present in the same crystal, and these elegant examples contain rigid ligands.[4] This article reports that the combination of silver(I) salts with the flexible, potentially tridentate ligand 2,6-$C_5H_3N\{C(=O)N(Me)$-4-$C_5H_4N\}_2$, **1**, gives the complexes $[Ag_2(\mathbf{1})_2][BF_4]_2$, **2**, and $[\{Ag_3(\mathbf{1})_2\}_n][CF_3SO_3]_{3n}$, **3**, which contains both macrocycles and polymers (**A** and **B**, Scheme 1) connected by bridging silver(I) ions and so gives insight into the structural changes that accompany ROP.

Crystalline samples of complexes **2** and **3** were prepared by slow diffusion of solutions of ligand **1** and the appropriate silver(I) salt.† The ^{1}H NMR spectra of complexes **2** and **3** in solution in dmf-d_7 at room temperature showed only a single set of ligand resonances, shifted from those of the free ligand, consistent with the presence of either a symmetrical structure in solution or with a less symmetrical fluxional system; low temperature NMR was not possible because the complexes had very limited solubility in suitable solvents. The ESI-MS, obtained from a cooled solution in acetonitrile, contained peaks corresponding $[Ag_n\mathbf{1}_nX_{n-1}]^+$ with maximum value of $n = 4$. For example **2** gave envelopes of peaks at m/z = 454, 995, 1536, and 2077 (n = 1–4 respectively, X = BF_4, reported for Ag^{107}, B^{11} isotopes). These data do not define the structures in solution, but they do indicate that oligomers are present in solution whereas extended structures are present in the solid state.

The structure of the dication in complex **2** is shown in Fig. 1.† The basic building block is a macrocycle, which contains an inversion centre and so is in the chair conformation. In the solid state, the macrocycles associate through secondary bonding between the silver(I) centres and the central pyridyl group, with the intermacrocycle distance Ag···N(22A) = 2.545(4) Å considerably longer than the intramacrocycle distances Ag–N(11) = 2.216(4) and Ag–N(34A) = 2.199(4) Å. Since each macrocycle contains two silver(I) acceptors and two pyridyl donors, there are four intermolecular interactions for each macrocycle, and this leads to formation of the unusual, tightly packed "sheet of macrocycles" structure shown in Fig. 1. The solvent molecules and anions lie in the spaces between the planes.

The remarkable structure of complex **3** is shown in Figs. 2 and 3.† There are 7 independent silver atoms in the structure and they can be divided into three sets. Atoms Ag(1) and Ag(2) are present in a macrocycle $[Ag_2(\mu\text{-}\mathbf{1})_2]^{2+}$ (Fig. 2), which is similar to the macrocycle present in complex **2**. The macrocycles also pack into



Scheme 1

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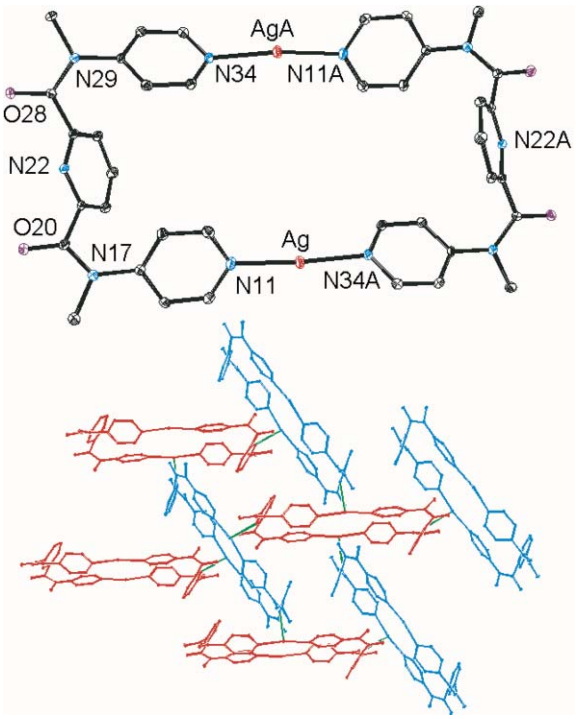

Fig. 1 The structure of complex **2**: above, an individual macrocycle and, below, the sheet of macrocycles.

planes (Fig. 2), though the intermacrocycle interactions now involve Ag···O=C interactions [Ag(1)···O(344) = 2.75, Ag(2)···O(324) 2.74 Å] which are much weaker than the Ag···N interactions in **2**. Atoms Ag(3), Ag(4) and Ag(5) are present in

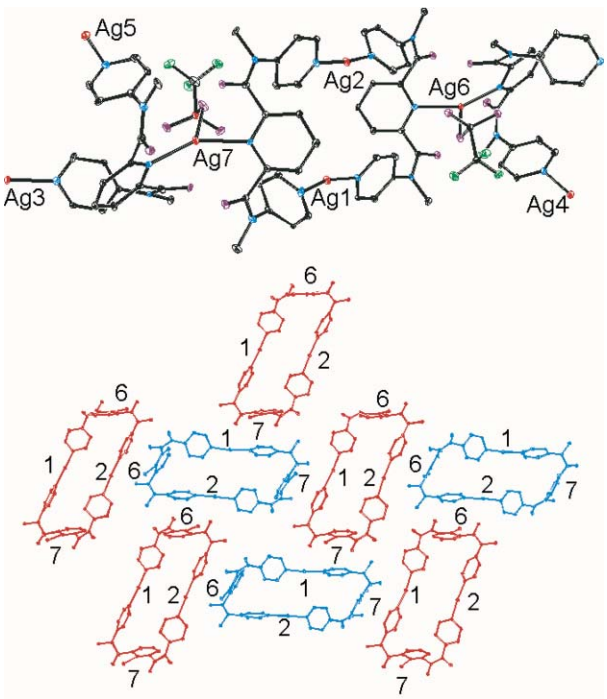

Fig. 2 Structure of the macrocycle in complex **3**: above, a single macrocycle and its connections to polymers on either side and, below, the plane of macrocycles.

polymer chains; Ag(4) and Ag(5) are located at centres of inversion and are present at half occupancy. Hence in the polymer chains $[\{Ag(\mu\text{-}\mathbf{1})\}_n]^{n+}$, the sequence is [–Ag(3)–**1**–Ag(4)–**1**–Ag(3)–**1**–Ag(5)–**1**–}$_n$, as shown in Fig. 3. The final silver atoms Ag(6) and Ag(7) act as links between the macrocycles and polymers by binding to a central pyridine group of each; they also bind to a triflate anion, and so have distorted trigonal geometry (Fig. 2), with additional secondary bonding to oxygen atoms of neighbouring carbonyl groups. The polymer chains pack parallel to one another (along the *a* axis) and are linked alternately to macrocycles in the sheet above and below (Fig. 3). Spaces between the polymer chains are occupied by solvent molecules and triflate anions. The overall network structure contains alternating sheets comprised of macrocycles and polymers, connected by bridging silver ions.

Since the macrocycles and polymer chains in complex **3** co-exist in the same lattice, and so must have similar energies, it is interesting to compare the conformations of the ligand **1** in the two forms, which can be considered as supramolecular isomers.[1–4] The narrow range of dihedral angles Me–N–C=O = 1–11° for all *N*-methyl amide units in complexes **2** and **3** define the stereochemistry as *cis,cis* for all ligands **1**.[5] The dihedral angle which varies most is that defining the orientation of the carbonyl group to the central pyridine ring in ligand **1**. In the macrocycle **2**, these dihedral angles N(22)–C(21)–C(19)–O(20) and N(22)–C(23)–C(27)–O(28) = −49 and 53°, respectively, define the conformation as distorted *cis,cis,syn* (Scheme 1), which is ideal for formation of a macrocycle.[5] Similar dihedral angles [45, −56 and 55, −39°] are seen for the macrocyclic components in complex **3**. However, for the polymer components in complex **3**, the corresponding pairs of dihedral angles [41, −117 and −40, 118°] define the conformation of the ligands **1** as distorted *cis,cis,anti* (Scheme 1). Thus, the ring-opening polymerization of the macrocycles can be considered to occur by cleavage of a silver–pyridyl bond, followed by rotation of

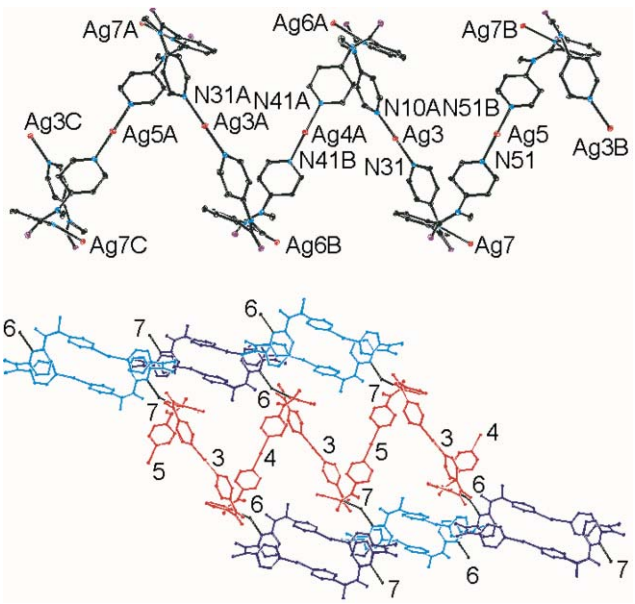

Fig. 3 The structure of the polymer units in complex **3**: above, an individual polymer chain and, below, the sandwich of the polymer between sheets of macrocycles above and below. The macrocycles are dark or light blue depending on whether they connect to the polymer through Ag(6) or Ag(7).

one of the amide groups to convert the ligand conformation from *cis,cis,syn* to *cis,cis,anti* and then aggregation steps to form the polymer, as indicated in Scheme 1. The combined studies by NMR, ESI-MS and X-ray structure determination support the view that in solution there is a dynamic equilibrium between macrocycles and ring-opened oligomers, and that the polymers form only during crystallization by aggregation at the crystal surface.[1] The process is significantly different than in complexes with rigid ligands when twisting about a metal–ligand bond is the key step.[4]

We thank the NSERC (Canada) for financial support. RJP thanks the Government of Canada for a Canada Research Chair.

Notes and references

† The synthesis of **2** was by reaction of $AgBF_4$ in thf with ligand **1** in CH_2Cl_2 in a 1 : 1 molar ratio. The synthesis of **3** was by reaction of AgOTf in thf with ligand **1** in CH_2Cl_2 in a 3 : 1 molar ratio. Analytical data for **2**: calc. for $C_{19}H_{17}AgBF_4N_5O_2$: C, 42.1; H, 3.2; N, 12.9. Found: C, 41.7; H, 3.3; N, 12.5%. X-Ray data: **2**·$2CH_2Cl_2$·thf, $C_{44}H_{46}Ag_2B_2Cl_4F_8N_{10}O_5$, FW = 1326.07, monoclinic, $P2_1/c$, a = 13.0047(7), b = 15.8034(8), c = 12.9509(5) Å, β = 103.229(3)°, V = 2591.0(2) Å^3, Z = 2, d_{calc} = 1.700 Mg m^{-3}, μ = 1.046 mm^{-1}, R_1 [$I > 2\sigma(I)$] = 0.044, wR_2 = 0.104. 2 × **3**·$5Me_2CO$, $C_{97}H_{98}Ag_6F_{18}N_{20}O_{31}S_6$, FW = 3221.53, monoclinic, $P2_1/c$, a = 24.0395(4), b = 14.8168(3), c = 42.3734(6) Å, β = 97.121(1)°, V = 14976.5(4) Å^3, Z = 4, d_{calc} = 1.429 Mg m^{-3}, μ = 0.942 mm^{-1}, R_1 [$I > 2\sigma(I)$] = 0.103, wR_2 = 0.272. There was evidence for additional disordered acetone molecules which were treated using the program SQUEEZE. CCDC 279074 and 279075. See http://dx.doi.org/10.1039/b510080a for crystallographic data in CIF or other electronic format. NMR data for **2** in dmf-d_7: δ(^{1}H) = 8.62 [m, 4H, C_5H_4N–$H^{2,6}$]; 8.15 [m, 1H, C_5H_3N–H^4]; 7.91 [m, 2H, C_5H_3N–$H^{3,5}$]; 7.44 [m, 4H, C_5H_4N–$H^{3,5}$]; 3.40 [s, 6H, Me].

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