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Ring-opening polymerization of gold macrocycles and self-assembly of a coordination polymer through hydrogen-bonding

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The equilibrium between digold and tetragold rings and a ring-opened oligomer and polymer is established by NMR and ESI-MS studies in solution and by structure determinations in the solid state; the polymer containing amide-derivatized ligands undergoes self-assembly through hydrogen bonding to give an ordered network.

Dynamic coordination chemistry can be a powerful method for the synthesis of hybrid organic–inorganic macrocycles or polymers with metals in the backbone structure, and there is great interest in learning how to further organize these macromolecules for building functional molecular materials.[1] A particularly promising method is to incorporate hydrogen bonding groups such as amide units into the ligands, taking advantage of the known patterns of self-assembly between such units.[2] Other secondary bonds, such as aurophilic interactions in gold(I) complexes, can be used in similar ways to form complex structures by self-assembly.[3] Ring-opening polymerization of gold(I) macrocycles can occur easily and has given rise to interesting polymers.[4,5] This article reports the first successful synthesis of a polymer in which the association between polymer chains mimics that of the free bis(amido)bipyridine ligand used in the self-assembly, and it also demonstrates the reversible ring expansion of strained gold(I) macrocycles.

The ligand 1,2-$C_6H_4(NHCO–4–C_5H_4N)_2$, **1**, can exist in the chiral conformations **A** and **B**, with C_2 symmetry, or in the achiral conformation **C**, with C_s symmetry (Chart 1).† In the solid state, **1** exists as alternating conformers **..A..B..A..B..** associated through intermolecular hydrogen bonds between amide groups of adjacent molecules of **1** [N(1)···O(1A) = 2.850(2) Å] to form a ribbon structure as shown in Fig. 1.

Reaction of **1** with the digold(I) complex $[Au_2(\mu\text{–PP})(O_2CCF_3)_2]$ occurred by displacement of the trifluoroacetate ligands by the pyridyl groups of **1**, as shown in Scheme 1, and crystallization gave two interesting products. The macrocyclic complex **2a** and the polymer **3b** were isolated when PP = $Ph_2P(CH_2)_3PPh_2$ or $Ph_2P(CH_2)_4PPh_2$ respectively (Scheme 1).

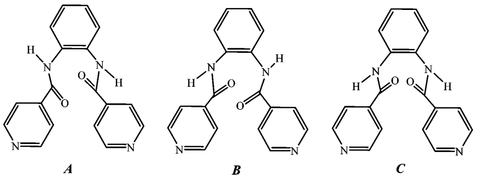


Chart 1 Conformations of ligand **1**.

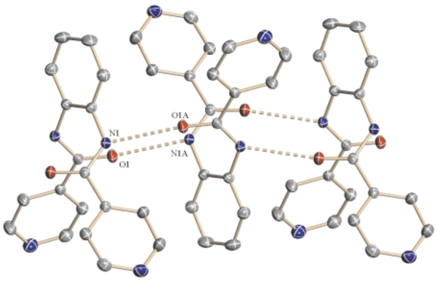
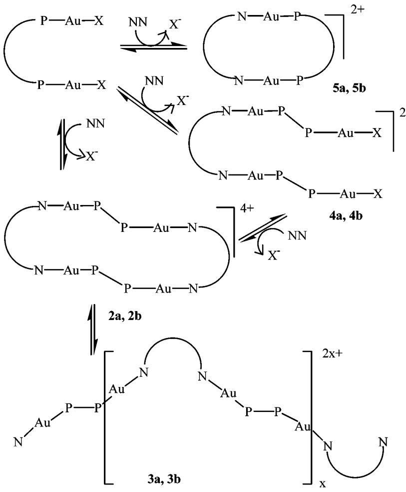


Fig. 1 The structure of the bis(pyridine) ligand **1**, showing the polymeric ribbon formed by intermolecular hydrogen bonding between amide groups.



Scheme 1 X = CF_3CO_2; NN = **1**; **2a–5a**, PP = $Ph_2P(CH_2)_3PPh_2$; **2b–5b**, PP = $Ph_2(CH_2)_4PPh_2$.

The structure of complex **2a** is depicted in Fig. 2, and contains the 42-membered double ring, $[Au_4(\mu\text{–PP})_2(\mu\text{–}\mathbf{1})_2]^{4+}$ tetracation, which adopts a step-like conformation. The ligands **1** adopt conformation **C** (Chart 1), and each pair of N–H groups is hydrogen bonded to an oxygen atom of a trifluoroacetate anion [N(4)···O(81) = 2.736(9) Å and N(3)···O(81) = 2.856(8) Å]. The remaining anions are involved in weak gold–oxygen interactions [Au(1)···O(92) = 2.97 Å] and hydrogen bonding with water molecules of crystallization [O(91)···O(7)

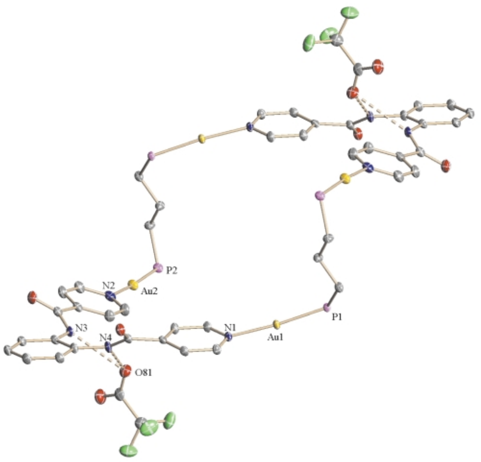


Fig. 2 The double ring structure of complex **2a**. Phenyl rings and anions not involved in hydrogen bonding have been removed for clarity.

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= 2.767(8) Å] (Fig. 2). There is no intermolecular hydrogen bonding present between amide groups of adjacent molecules.

The structure of complex **3b** is shown in Fig. 3a and 3b. The complex exists as polymeric cations with repeat units $[\{–\mathbf{1}–\text{Au}–\text{PP}–\text{Au}–\}_x]^{2x+}$ (Fig. 3a), that further associate through interchain amide hydrogen bonds to give a three-dimensional network (Fig. 3b). In each polymer chain, the ligands **1** exist in the chiral conformations **A** and **B**, alternating, as $\{–\mathbf{1A}–\text{AuPPAu}–\mathbf{1B}–\text{AuPPAu}–\}_x$, in the zig-zag chains that are oriented along the *a*-axis (Fig. 3b). Hydrogen bonding occurs between the amide groups of the bis(pyridyl) ligands in a manner analogous to that in the free ligand **1** (Fig. 1). Thus, each **A** unit of a chain is sandwiched between **B** units of two adjacent chains and each **B** unit is similarly positioned between **A** units of two other chains. The self-assembly of the chains through hydrogen bonding occurs to form **..A..B..A..B..** ribbons along the *c*-axis (Fig. 3b). Since the zig-zag chains overlap the chains both above and below, propagation of the network along the *b*-axis occurs naturally, to give a three-dimensional network (Fig. 3b). This remarkable network structure, with its intricate array of hydrogen bonding interactions, can be considered to result from crystal engineering of the polymer, since the conformation and hydrogen bonding between the coordinated ligands $[\text{N}(9)\cdots\text{O}(8\text{A}) = 2.73(1)$ Å] in **3b** (Fig. 3b) are so similar to those in the free ligand **1** (Fig. 1).

The remarkable difference in the structures of **2a** and **3b**, resulting from a difference in just one methylene spacer group in the diphosphine ligand, prompted a study of the structures in solution. At 293 K the ^{31}P NMR spectrum of a solution of **2a** in CD_2Cl_2 contained a single broad resonance ($\delta = 23.68$), which resolves at 233 K to give a broad singlet ($\delta = 25.07$) assigned to **2a** and two equal intensity resonances ($\delta = 24.11, 23.64$) assigned to **4a** (Scheme 1). The identity of **4a** was deduced from the ESI-MS of a solution of **2a** in dichloromethane–methanol, which showed major peaks at $m/z = 2269$ and at 319, corresponding to $[\mathbf{4a}\cdot CF_3CO_2]^+$ and $[\mathbf{1}\cdot H]^+$ respectively. Complex **4a** is formed by displacement of one equivalent of ligand **1** from **2a** by two trifluoroacetate anions. Similarly, the ^{31}P NMR spectrum of complex **3b** at room temperature contained a single resonance ($\delta = 25.84$) but, at 233 K, the peak splits to give a major singlet at $\delta = 26.3$ assigned to **2b**, two low intensity resonances at $\delta = 26.0$ and 27.5 assigned to **4b**, and a singlet at $\delta = 29.4$ assigned to **5b**. The ESI-MS contained major peaks at $m/z = 2296$ and at 319, corresponding to $[\mathbf{4b}\cdot CF_3CO_2]^+$ and $[\mathbf{1}\cdot H]^+$ respectively. The highest mass peak observed was at $m/z = 2541$ corresponding to $[\mathbf{2b}\cdot(CF_3CO_2)_2(HF_2)]^+$ and, in this case, there was also a significant peak at $m/z = 1251$ for the simple ring $[\mathbf{5b}\cdot CF_3CO_2]^+$. Thus, although the solid state structures are very different for the complexes with PP = $Ph_2P(CH_2)_nPPh_2$, with $n = 3$ or 4, the solution state structures are similar. The only significant difference is that the simple ring complex **5** (Scheme 1) is relatively favoured with the diphosphine with the longer spacer group.[6]

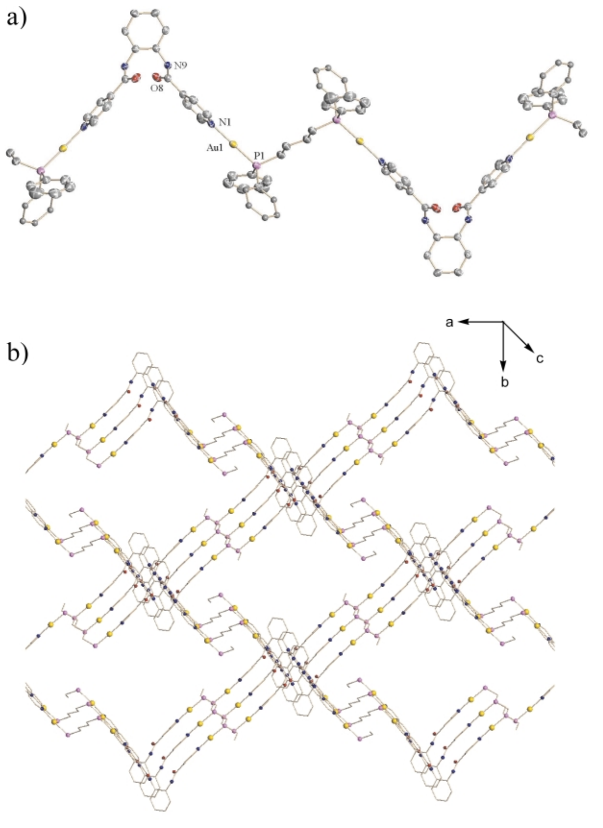

Fig. 3 a) The structure of the cationic zig-zag polymer **3b**. b) The 3-D network formed by hydrogen bonding between amide groups. Phenyl rings have been removed for clarity.

In conclusion, this work has shown that the dynamic exchange between trifluoroacetate and bis(pyridine) ligands allows easy interconversion of ring, double ring and ring-opened complexes. The ring–double ring interconversion is established for the first time in these examples. Slow crystallization gives single crystals of the double ring and the ring-opened polymer, with the different diphosphine ligands. The polymer is not present in significant concentration in solution and evidently forms upon crystallization. Most significantly, this is the first time that crystal engineering has been successful in organizing the polymer chains in the solid state through interchain hydrogen bonding that closely mimics the hydrogen bonding in the parent bis(pyridine) ligand **1**. As a result, the polymer **3b** has a beautiful solid-state network structure (Fig. 3).

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Notes and references

† Crystal data: **1**:$C_{18}H_{14}N_4O_2$, $M = 318.33$, monoclinic, $C2/c$, $a = 17.5572(7)$, $b = 9.2062(4)$, $c = 9.6370(5)$ Å, $\beta = 102.981(2)°$, $V = 1517.87(12)$ Å^3, $Z = 4$, $R1 = 0.0560$, $wR2 = 0.1160$ for data with $I > 2\sigma(I)$ at 200 K; **2a**·$2H_2O$: $C_{98}H_{84}Au_4F_{12}N_8O_{14}P_4$, $M = 1372.77$, triclinic, $P\bar{1}$, $a = 10.55(3)$, $b = 11.73(4)$, $c = 19.52(6)$ Å, $\alpha = 98.94(5)$, $\beta = 90.26(5)$, $\gamma = 102.28(5)°$, $V = 2329(12)$ Å^3, $Z = 2$, $R1 = 0.0408$, $wR2 = 0.0966$ for data with $I > 2\sigma(I)$ at 100 K; **3b**·$CHCl_3$·H_2O: $C_{101}H_{84}Au_4Cl_3F_{12}N_8O_{13}P_4$, $M = 2863.86$, monoclinic, $C2/c$, $a = 34.4646(8)$, $b = 21.6440(5)$, $c = 9.3190(2)$ Å, $\beta = 100.011(1)°$, $V = 6845.7(3)$ Å^3, $Z = 2$, $R1 = 0.0789$, $wR2 = 0.2334$ for data with $I > 2\sigma(I)$ at 200 K. CCDC 212393–212395. See http://www.rsc.org/suppdata/cc/b3/b306004g/ for crystallographic files in CIF format.

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6 The separation between pyridyl nitrogen donors in **1** = 8.40, **2a** = 8.71, **3b** = 8.84 Å are similar but molecular modeling indicates that this distance would need to be considerably less in the simple ring structures **5a** = 6.4 and **5b** = 7.1 Å, with resultant angle strain. The ring-opening to give the double ring **2** or polymer **3** relieves the angle strain.