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Self-Assembly of Coordination Polymers: Evidence for Dynamic Exchange between Oligomers in Solution and the Isolation of a Homochiral Decagold(I) Oligomer

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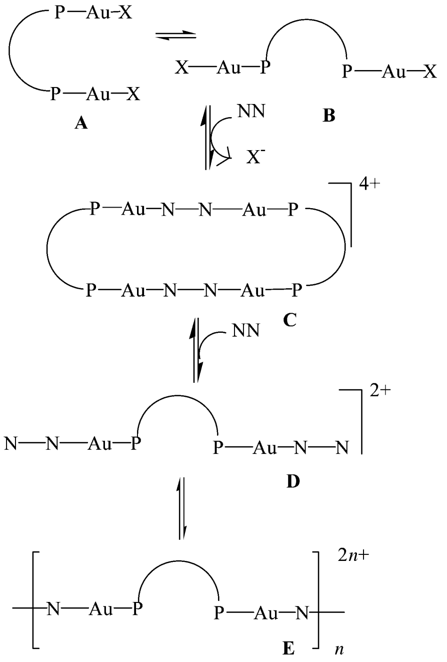
Metal-containing polymers can have interesting redox, optical, electronic, or catalytic properties, and so the synthesis and study of these hybrid organic−inorganic materials is an active area of research.[1] These materials may have applications for separation, storage, and heterogeneous catalysis.[2] For example, chiral porous networks formed from helical polymeric chains have potential as materials for asymmetric catalysis or for chiral sensing and separation.[3] Polymers can often be formed by self-assembly on combination of a labile metal precursor complex with one or more bridging bidentate ligands.[4] The use of gold(I) as the metal center, with diphosphines and other bidentate ligands as bridging groups, has given insights into the self-assembly process, as illustrated in Scheme 1. Depending on the flexibility and preferred conformation of the bridging ligands, there can be an easy exchange between cyclic and open chain oligomers in solution, and high molecular weight polymers can be formed on crystallization.[4,5] Macrocyclic complexes (**C**) and polymers (**E**, n = infinity) have been isolated previously, but the isolation of the ring-opened oligomer (**E**, $n = 5$) reported now is unprecedented and can be considered as a missing link in the ring-opening polymerization process (Scheme 1).[5]

In the present work, the chiral diphosphine ligand 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) was used in making the precursor molecules $[Au_2(\mu\text{-}R,S\text{-BINAP})(O_2CCF_3)_2]$, **1a**, and $[Au_2(\mu\text{-}S\text{-BINAP})(O_2CCF_3)_2]$, **1b**. Reaction of **1a** or **1b** with the easily exchanged linear bis(pyridine) ligand 1,2-*trans*-bis(4-pyridyl)ethylene (bipyen), followed by crystallization from CH_2Cl_2/pentane, gave the polymeric complex $[\{Au_2(\mu\text{-}R\text{-BINAP})_{0.5}(\mu\text{-}S\text{-BINAP})_{0.5}(\mu\text{-bipyen})\}_n](CF_3CO_2)_{2n}$, **2a**, or the remarkable oligomeric $[Au_{10}(\mu\text{-}S\text{-BINAP})_5(\mu\text{-bipyen})_4(\kappa^1\text{-bipyen})_2](CF_3CO_2)_{10}$, **3**. These syntheses are reproducible, and the products **2a** and **3** are isolated as white, air-stable crystals. The chiral polymer $[\{Au_2(\mu\text{-}S\text{-BINAP})(\mu\text{-bipyen})\}_n](CF_3CO_2)_{2n}$ **2b** was prepared by crystallization from acetone solution. The structures of the racemic polymer **2a**, chiral polymer **2b**, and chiral oligomer **3** are shown in Figure 1.

The structures of the hetero- and homochiral polymers **2a** and **2b** are shown in Figure 1a,b (trifluoroacetate anions and solvate molecules are not shown). In **2a**, the configuration of the bridging BINAP ligands is strictly alternating along the chain, and the conformation of the binaphthyl group [BINAP torsion angle 95°, Au(1)···Au(2) = 3.92 Å] disfavors formation of a macrocycle of type **C** (Scheme 1). The $[Au_{10}(\mu\text{-}S\text{-BINAP})_5(\mu\text{-bipyen})_4(\kappa^1\text{-bipyen})_2]^{10+}$ cations in complex **3** (Figure 1c) contain 10 gold atoms, 5 bridging *S*-BINAP ligands, 4 bridging bipyen ligands, and 2 terminal monodentate bipyen ligands. The torsion angles of the BINAP ligands in the crystal structure range from 93 to 117.4°, and the corresponding Au···Au distances are 4.42−4.66 Å. The BINAP ligands in **2** and **3** are too bulky to allow interchain Au···Au bonding.[3]

Scheme 1. Gold(I) Complexes with Alternating Flexible Diphosphine (PP) and Linear Bis(pyridine) (NN) Ligands Formed by Displacement of Trifluoroacetate (X) Ligands in the Precursor Molecule (**A** or **B**), Showing the Equilibrium between Cyclic Complex (**C**) and Ring-Opened Complex (**D**) or Oligomer or Polymer (**E**)



It is often assumed that coordination polymers undergo partial degradation to linear or cyclic oligomers in solution.[1−4] However, the equilibria in solution are often difficult to characterize. The isolation of oligomeric **3** suggested that similar oligomeric fragments might exist in solution, and confirmation through the use of electrospray mass spectrometry (ESI-MS) and low-temperature ^{31}P NMR spectroscopy was attempted.

The ^{31}P NMR spectrum in CD_2Cl_2 solution of chiral **3** contained a single peak at room temperature ($\delta = 23.3$). However, at lower temperatures, the peak broadened and then split into three separate peaks. At −60 °C, the three peaks appear at $\delta = 22.9$, 26.4, and 33.4, with relative integration values of 3:1:1, respectively. The more intense peak at $\delta = 22.9$ is tentatively assigned to the inner BINAP ligands, while the less intense peaks are assigned to the nonequivalent phosphorus atoms of the outer BINAP ligands of oligomeric fragments. The integration ratios thus correspond to an average oligomer chain length of 5 BINAP ligands, or 10 gold atoms. Similar spectra were observed for the racemic complex **2a** in solution [$\delta(P) = 22.7$, 26.2, and 33.2 at −60 °C].

The NMR spectra of **3** do not discriminate between the presence of a single Au_{10} oligomer in solution or an assembly of oligomers with this average number of gold atoms. The ESI-MS spectra of **2**

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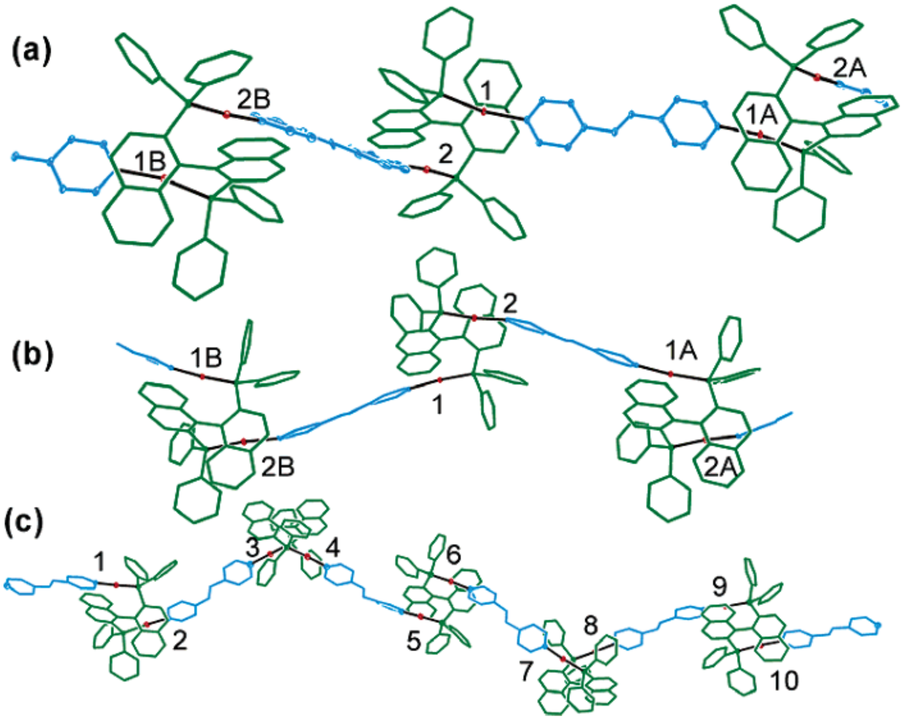

Figure 1. Structures of complexes **2** and **3**: (a) a section of the heterochiral polymeric chain of **2a**, showing a section with *R,S,R* sequence of BINAP ligands; (b) a similar section of the homochiral polymeric chain of **2b**, showing a *S,S,S* sequence of BINAP ligands; (c) the Au_{10} oligomer **3** with *S*-BINAP groups. Only the gold atoms (red) are numbered; BINAP and bipyen ligands are color-coded green and blue, respectively.

and **3**, recorded for solutions in CH_2Cl_2, are similar and indicate the presence of an assembly of oligomers. Thus, for **3**, the following peaks with tentative assignments were observed: $m/z = 2463$, $[Au_{16}(PP)_8(NN)_7(TFA)_4\text{-}8H]^{4+}$; 4327, $[Au_{14}(PP)_7(NN)_6(TFA)_4\text{-}8H]^{2+}$; 1841, $[Au_{12}(PP)_6(NN)_7\text{-}8H]^{4+}$; 3706, $[Au_{12}(PP)_6(NN)_6(TFA)_2\text{-}8H]^{2+}$; 3084, $[Au_{10}(PP)_5(NN)_6\text{-}8H]^{2+}$; 1311, $[Au_2(PP)(NN)(TFA)]^{+}$; 1129, $[Au_2(PP)(TFA)]^{+}$; 690, $[Au_2(PP)(NN)_2]^{2+}$ {PP = BINAP, NN = bipyen; TFA = trifluoroacetate). These data indicate the presence of oligomers containing up to 16 gold atoms in solution.

These combined NMR and ESI-MS data for both **2** and **3** support the interpretation that, in dichloromethane solution at room temperature, there is dynamic exchange between a large array of oligomeric gold(I) complexes and that this exchange can be slowed at low temperature. The complex equilibrium is expected to vary with temperature, solvent, and concentration. Because the equilibria for **2a** and **3** in dichloromethane solution are similar, the different behavior on crystallization of **2a** (polymer) and **3** (oligomer) is related to the difference in solubility between the oligomeric and polymeric forms in each case. Both structures of **2a** and **3** are porous and contain dichloromethane solvate molecules. Just changing solvents from dichloromethane to acetone allows crystallization of the chiral polymer **2b** in place of the oligomer **3**. The characterization of the oligomer **3** is a significant step in understanding the polymerization of labile coordination compounds. It is possible that larger or smaller oligomers might crystallize from other solvent media, and ongoing investigations of the system are aimed at the isolation of further intermediates in the polymerization reaction.

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Supporting Information Available: Experimental details for the synthesis and characterization of complexes **1**−**3**. Details of the X-ray structure determinations for complexes **2a**·$2.65CH_2Cl_2$, **2b**·3acetone, and **3**·$10.5CH_2Cl_2$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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