DOI: 10.1002/anie.200701325

Coordination Polymers

# A Coordination Polymer of Gold(I) with Heterotactic Architecture and a Comparison of the Structures of Isotactic, Syndiotactic, and Heterotactic Isomers**

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The kinetically controlled polymerization of prochiral or racemic (*R*/*S*) organic monomers may often give polymers with atactic (random chirality), isotactic (*R,R,R*/*S,S,S*), or syndiotactic (*R,S,R,S*) architecture, but formation of the heterotactic (*R,R,S,S*) architecture is rare because it requires monomer recognition of the chirality of both the ultimate and penultimate units of the growing polymer chain.[1] The heterotactic architecture is more commonly obtained by polymerization of racemic monomers, such as lactides, which contain two asymmetric centers (*R,R*/*S,S*).[2] The thermodynamically controlled formation of coordination polymers from racemic (*R*/*S*) ligands has given crystalline solids containing either isotactic or syndiotactic architectures (usually termed homochiral or heterochiral polymers in the coordination polymer literature), but there appear to be no reported examples of coordination polymers with heterotactic architecture (the atactic architecture is incompatible with the single-crystalline state and so is also absent).[3,4] Herein the first hybrid organic–inorganic polymer with the heterotactic architecture is reported, as well as the first direct structural comparison of coordination polymers with the isotactic, syndiotactic, and heterotactic architectures.[5]

It is already known that gold(I) centers, with their predictable linear geometry and high reactivity towards ligand substitution, are valuable for building coordination polymers, and structurally characterized coordination polymers, derived by self-assembly from a racemic bridging ligand, have been isolated in both syndiotactic (heterochiral, *R,S,R,S*) and isotactic (homochiral, *S,S,S*) architectures.[6] In the present work, the chiral ligand 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (binap) was used to make building-block precursor molecules as either single enantiomers $[Au_2(\mu\text{-}S\text{-binap})X_2]$ (**1a**, $X = CF_3CO_2$; **1b**, $X = NO_3$) or as a racemic mixture $[Au_2(\mu\text{-}R,S\text{-binap})X_2]$ (**1c**, $X = CF_3CO_2$; **1d**, $X = NO_3$). Polymers were then assembled by linking the digold units in molecules **1a**–**1d** by displacement of the weakly bound trifluoroacetate or nitrate ions by the linear ligand 4,4′-bipyridine (bipy), and subsequent crystallization gave the corresponding (solvated) cationic polymers **2**–**5**, respectively, of general formula $[\{Au_2(\mu\text{-binap})(\mu\text{-bipy})\}_n](X)_{2n}$. Crystals of X-ray quality were grown for the polymers **2** (*S*-binap, $X = CF_3CO_2$), **4** (*R*/*S*-binap, $X = CF_3CO_2$), and **5** (*R*/*S*-binap, $X = NO_3$), and the structures of the polymeric cations are shown in Figure 1.[7] Most remarkably, complex **5** has the unprecedented heterotactic (*R,R,S,S*) architecture of binap ligands, while **4** has the more common syndiotactic (*R,S,R,S*) architecture and **2** necessarily has the isotactic (*S,S,S*) architecture. Figure 1 therefore shows, for the first time, a direct structural comparison of the isotactic, syndiotactic, and heterotactic isomers of a polymer.

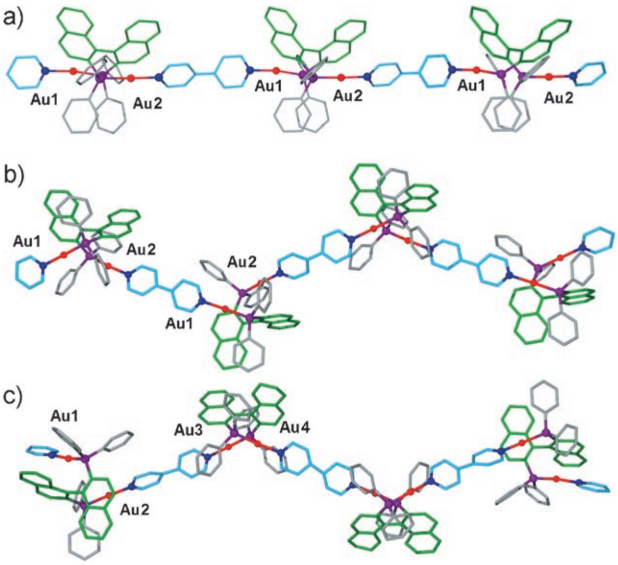

***Figure 1.*** Structures of complexes **2**, **4**, and **5**: a) a section of the homochiral polymer chain of **2** showing the *S,S,S* sequence of the binap ligands; b) a section of the heterochiral polymer structure of **4** showing the *R,S,R,S* sequence of the binap ligands; c) a section of the heterochiral polymer **5** showing an *S,S,R,R* sequence of binap ligands. Naphthyl units green, bipy ligands blue, Ph gray, Au red, P purple.

It can be seen by inspection of Figure 1 that the isotactic polymer **2** is more linear while the syndiotactic and heterotactic polymers **4** and **5** are more zigzag in structure. This observation is confirmed by the length of a repeat $\{Au_4(\mu\text{-binap})_2(\mu\text{-bipy})_2\}$ unit, which follows the sequence **2** (31.2 Å) > **4** (25.8 Å) > **5** (24.3 Å), while the polymer chain diameter follows the opposite sequence **2** (15.3 Å) < **4** (18.6 Å) < **5** (20.2 Å).

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[**] We thank the NSERC (Canada) for financial support and for a scholarship to C.A.W., and the Government of Canada for a Canada Research Chair to R.J.P.

The polymers **2**–**5** dissolve in $CD_2Cl_2$, breaking down to form oligomers, which can be partially characterized by ESI-MS and low-temperature $^{31}$P NMR spectroscopy.[6a] The data indicate that the average size of oligomer units in solution is greater for *S*-binap compared to racemic binap, for trifluoroacetate compared to nitrate derivatives, and at −20 °C compared to at room temperature. Thus the highest mass identified for each compound followed the sequence **2** (*m*/*z* 6799, $[Au_{10}(PP)_5(NN)_5(tfa)_8(Cl)-1H]^+$) > **3** (2413, $[Au_4(PP)_2(NN)_2(Cl)_2-1H]^+$) > **4** (2293, $[Au_3(PP)_2(NN)_2(tfa)(Cl)-1H]^+$) > **5** (1234, $[Au_2(PP)(NN)(NO_3)]^+$; PP = binap, NN = 4,4′-bipy, tfa = trifluoroacetate). The $^{31}$P NMR spectra, in $CD_2Cl_2$ at −20 °C, of the nitrate derivatives **3** and **5** each give three resonances (**3**: $\delta = 21.61$, 25.08, 30.96 ppm with relative intensities 1:1:3; **5**: $\delta = 21.58$, 25.03, 30.85 ppm with relative intensities 1:1:0.75). The peak with the highest value of $\delta$ is assigned to the $^{31}$P atoms of internal binap units while those at lower $\delta$ values are assigned to the terminal binap groups.[6,8] The data indicate an average oligomer size of 10 and 5.5 gold atoms in **3** and **5**, respectively, again indicating a higher degree of aggregation with the *S*-binap ligand under these conditions. The trifluoroacetate derivatives **2** and **4** each gave only a single $^{31}$P NMR resonance under similar conditions, indicating fast exchange between the bipy and tfa ligands, and so it was not possible to estimate the oligomer sizes in solution.

The spectroscopic data indicate that there are significant differences in the solution behavior of the trifluoroacetate and nitrate derivatives **4** and **5**, both in terms of rates of ligand substitution and average oligomer size (**4** > **5** in each case), but it is still not easy to understand why **4** and **5** crystallize with the syndiotactic and heterotactic architectures, respectively. In the solid-state structures, the anions are not coordinated to gold(I) (the shortest contact is $d(Au\cdots O) = 3.49$ Å in **4**) and so it is likely that cation–anion association is also weak in solution. Once a crystal seed is formed, in the presence of a dynamic mixture of oligomers in solution, the subsequent growth is controlled by the crystal surface acting as a template with resulting very high selectivity. Clearly much more research is needed to understand the details of the process.

In summary, we report the first structural characterization of a heterotactic coordination polymer, and the first structural comparison of isotactic, syndiotactic, and heterotactic isomers of any polymer. The switch from syndiotactic to heterotactic architecture is dependent on the anion used (trifluoroacetate versus nitrate). Ongoing investigations will be aimed at the isolation of further gold(I) polymers, with alternating linear-bridging bipy ligands in combination with racemic *R*/*S*-binap ligands, using a wider range of weakly coordinating anions. The aim is to understand better how the formation of syndiotactic versus heterotactic architectures can be controlled by choice of anion.

## Experimental Section

**2**: A filtered solution of $[Au_2(\mu\text{-}S\text{-binap})(CF_3CO_2)_2]$ (0.092 mmol), prepared from $[Au_2(\mu\text{-}S\text{-binap})Cl_2]$ (0.100 g, 0.092 mmol) and $AgCF_3CO_2$ (0.041 g, 0.184 mmol) in $CH_2Cl_2$ (10 mL), was added to a solution of 4,4′-bipy (14.4 mg, 0.092 mmol) in dichloromethane (10 mL). The mixture was stirred for 2 h, and the solvent was removed to give the product, which was dissolved in a minimum of $CH_2Cl_2$ and $CH_3OH$ and precipitated by addition of pentane. Yield: 87 %; $^{31}$P NMR (162 MHz, 293 K, $CD_2Cl_2$): $\delta = 18.31$ ppm. Elemental analysis (%) calcd for $C_{58}H_{40}Au_2P_2N_2O_4F_6$: C 49.80, H 2.84, N 2.00; found: C 49.51, H 2.88, N 2.06.

**3**: This complex was prepared similarly from $[Au_2(\mu\text{-}S\text{-binap})(NO_3)_2]$. Yield: 90 %; $^{31}$P NMR (162 MHz, 293 K, 1:1 $CD_2Cl_2$/$CD_3OD$): $\delta = 28.75$, 24.51, 21.83 ppm. Elemental analysis (%) calcd for $C_{54}H_{40}Au_2P_2N_2O_6$: C 50.01, H 3.11, N 4.32; found: C 50.33, H 2.94, N 4.38.

**4**: This complex was prepared similarly from $[Au_2(\mu\text{-}R/S\text{-binap})(CF_3CO_2)_2]$. Yield: 63 %; $^{31}$P NMR (162 MHz, 293 K, $CD_2Cl_2$): $\delta = 18.27$ ppm. Elemental analysis (%) calcd for $C_{58}H_{40}Au_2P_2N_2O_4F_6$: C 49.80, H 2.84, N 2.00; found: C 50.13, H 2.76, N 2.33.

**5**: This complex was prepared similarly from $[Au_2(\mu\text{-}R/S\text{-binap})(NO_3)_2]$. Yield: 66 %; $^{31}$P NMR (162 MHz, 293 K, 1:1 $CD_2Cl_2$/$CD_3OD$): $\delta = 30.21$, 25.49, 23.01 ppm. Elemental analysis (%) calcd for $C_{54}H_{40}Au_2P_2N_2O_6$: C 50.01, H 3.11, N 4.32; found: C 49.89, H 2.83, N 3.85.

X-ray structure analysis was carried out on a Nonius Kappa-CCD diffractometer ($Mo_{K\alpha}$ radiation), data collection and refinement were performed with SHELXTL V6.1, and an empirical absorption correction was applied.[7]

Received: March 26, 2007

**Keywords:** chirality · gold · polymers · self-assembly · supramolecular chemistry

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[7] **2**: $C_{58}H_{40}Au_2F_6N_2O_4P_2$, $M_r = 1398.82$, orthorhombic, space group $C222_1$, $Z = 8$, $a = 11.8033(3)$, $b = 28.8564(4)$, $c = 38.3325(9)$ Å, $V = 13056.1(5)$ Å$^3$, $\mu(Mo_{K\alpha}) = 0.71073$ Å, $T = 150(2)$ K, 21457 reflections collected, 11503 unique, $R_1(I>2\sigma I) = 0.0425$, $wR_2 = 0.1246$. **4**: $C_{61.50}H_{51}Au_2Cl_3F_6N_2O_6P_2$, $M_r = 1590.27$, orthorhombic, space

group *Pbca*, $a = 14.6995(2)$, $b = 25.8284(3)$, $c = 32.3400(4)$ Å, $V = 12\,278.4(3)$ Å$^3$, $\mu(\mathrm{Mo}_{K\alpha}) = 0.71073$ Å, $T = 150(2)$ K, 40220 reflections collected, 10836 unique, $R_1(I>2\sigma I) = 0.0476$, $wR_2 = 0.1321$. **5**: $C_{112.7}H_{89.4}Au_4N_8P_4O_{12}Cl_{4.7}$, $M_r = 2826.15$, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 20.540(4)$, $b = 24.291(5)$, $c = 27.441(6)$ Å, $\beta = 111.67(3)°$, $V = 12\,723(4)$ Å$^3$, $\mu(\mathrm{Mo}_{K\alpha}) = 0.71073$ Å, $T = 150(2)$ K, 36558 reflections collected, 20008 unique, $R_1(I>2\sigma I) = 0.0867$, $wR_2 = 0.2100$. Note: The SQUEEZE procedure of the PLATON software suite was used to account for the disordered anion and solvent electron density of **2** and **5**. This procedure accounted for a single $CF_3CO_2^-$ anion per asymmetric unit of **2** and a total of four $NO_3^-$ anions and 2.35 dichloroethane molecules per asymmetric unit of **5**. CCDC-641696–641698 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[8] The $^{31}$P NMR resonances are too broad to allow resolution of peaks for specific triads *S,S,S*, *S,R,S*, *S,S,R*.