

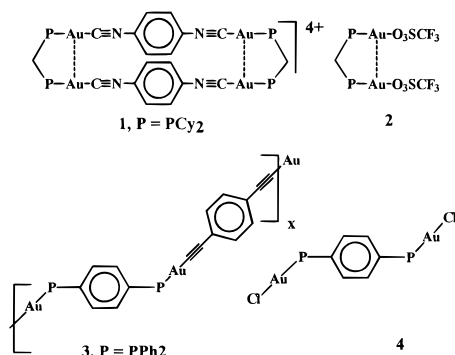
Linear Gold(I) Coordination Polymers: A Polymer with a Unique Sine Wave Conformation

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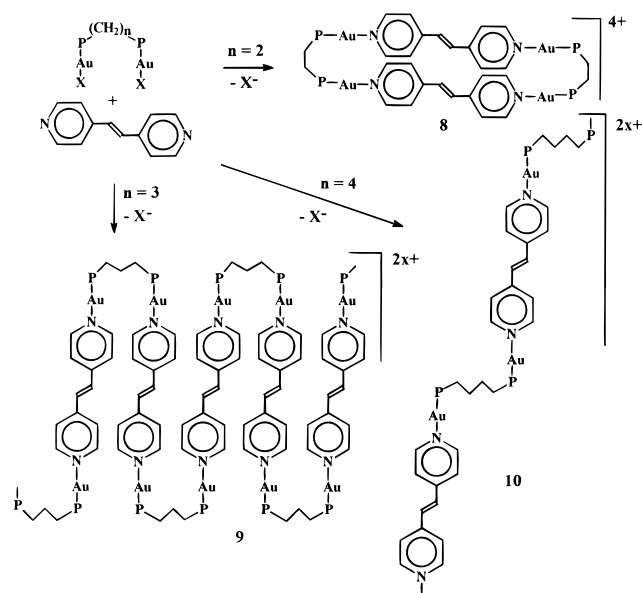
It is now well established that weak intra- and intermolecular bonding interactions between gold(I) centers can give rise to unusual molecular conformations and crystal packing, but the discovery of new structural types has usually been serendipitous and the tailored engineering of supramolecular structures, which may have new and interesting properties as advanced materials, is still in its infancy.^{1–6} One example of controlled synthesis, is the selective formation of gold(I) rings **1** from a precursor molecule **2** which is preorganized with *syn*-gold(I) centers, due to intramolecular Au···Au bonding with the short-bite diphosphine ligand Cy₂PCH₂PCy₂ (Cy = cyclohexyl),⁷ but formation of polymers **3** from a precursor molecule (**4**) with *anti*-gold(I) centers, where intramolecular Au···Au bonding is impossible.⁸ It is then natural to ask the question: when will the crossover from ring to polymer occur in synthesis from precursors [(CH₂)_n(PPh₂AuX)₂], in which the shortest intramolecular Au···Au contact will naturally increase with the value of *n*?⁹ This paper reports results from this study, in which the largest gold(I) ring yet known and a unique sine wave polymer have been prepared and structurally characterized.



In order to obtain crystalline polymers, the weakly bonding, rigid-rod ligand *trans*-1,2-bis(4-pyridyl)ethylene was used, on the basis that coordination of the N-donors to gold(I) would be

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Scheme 1^a



^a X = CF₃CO₂, P = PPh₂.

reversible and allow the ordered buildup of a polymeric structure, where the most thermodynamically stable geometry can be maintained,¹⁰ whereas more strongly binding bridging ligands give less ordered, insoluble polymers due to irreversible binding.^{3,8} The reaction of *trans*-1,2-bis(4-pyridyl)ethylene with [(CH₂)_n(PPh₂AuO₂CCF₃)₂] (**5**, *n* = 2; **6**, *n* = 3; **7**, *n* = 4) in tetrahydrofuran at room temperature occurred with displacement of trifluoroacetate to give the cationic complexes **8–10** (Scheme 1) which were isolated as colorless, air-stable solids. The compounds, including the polymers, are soluble in a 1:1 mixture of either CH₂Cl₂/MeOH or nitrobenzene/MeOH. They have good thermal stability and melt sharply with immediate decomposition at 228, 221, and 247 °C for **8**, **9**, and **10**, respectively, as determined by differential scanning calorimetry. Since the diphosphine backbone contains saturated carbon atoms, the compounds are all electrical insulators, with conductivities of (2–10) × 10^{−9} Ω^{−1}cm^{−1} as pressed disks.

The analytical and spectroscopic data for **8–10** do not distinguish between the possible ring or polymeric structures,¹¹ and so they were characterized by X-ray structure determinations.¹² Preliminary data for complex **8** show that it contains a 32-membered ring containing four gold(I) atoms (Supporting Information),¹² a structure which is analogous to that of the 26-membered ring reported for [(Au-C≡NC₆H₄N≡C-Au)₂(μ-Cy₂-PCH₂PCy₂)₂]⁴⁺ (**1**).⁷ The transition from ring to polymer occurs in **9** and **10**, and their structures are shown in Figure 1.

Both complexes have the expected linear gold(I) centers, each coordinated by a phosphorus and a nitrogen atom of the bridging diphosphine and bis(4-pyridyl)ethylene ligands, but the conformations of the resultant one-dimensional polymers are

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(11) Selected spectroscopic data (NMR in CD₂Cl₂/CD₃OD). For **8**: δ(³¹P) = 28.94 (s); δ(¹H) = 8.62 [d, 8H, *o*-H, py], 7.89 [d, 8H, *m*-H, py], 7.42–7.68 [m, 44H, Ph, CH=CH], 2.69 [m, 8H, CH₂]. For **9**: δ(³¹P) = 25.43 (s); δ(¹H) = 8.69 [d, 4H, *o*-H, py], 7.94 [d, 4H, *m*-H, py], 7.31–7.66 [m, 22H, Ph, CH=CH], 2.33 [m, 4H, CH₂], 1.62 [m, 2H, CH₂]. For **10**: δ(³¹P) = 25.6 (s); δ(¹H) = 8.63 [d, 4H, *o*-H, py], 7.91 [d, 4H, *m*-H, py], 7.48–7.76 [m, 22H, Ph, CH=CH], 2.73 [m, 4H, CH₂], 1.94 [m, 4H, CH₂]. Note that the complexes only dissolve in polar solvent mixtures and the structures in solution may differ from those determined in the solid state. In particular, the polymers appear to break down into smaller fragments and the solutions do not exhibit the viscosity expected for polymers; the ³¹P NMR spectrum of **10** at −90 °C contains three sharp peaks at δ(P) = 23.4, 26.8, and 27.1, probably indicating the presence of at least two rapidly equilibrating species.

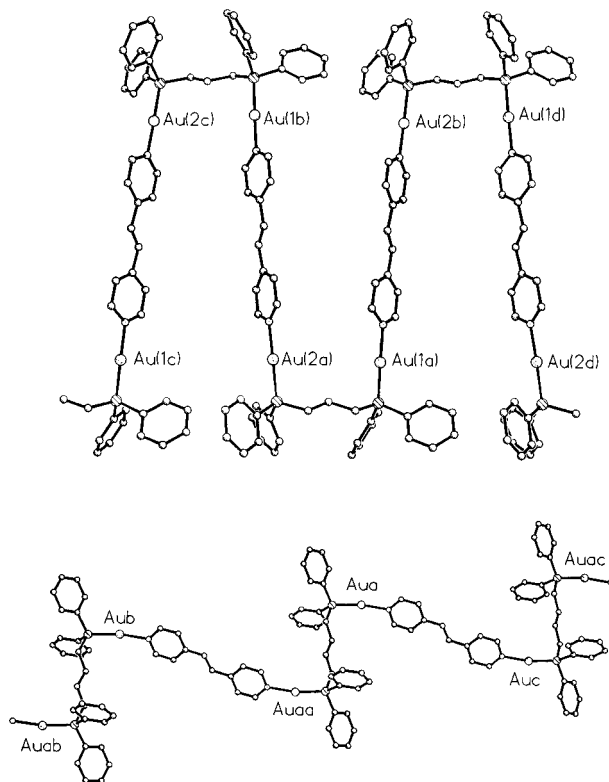


Figure 1. Views of the structures of the cationic polymers $[\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2-\text{Au}-\text{NC}_5\text{H}_4\text{CH}=\text{CHC}_5\text{H}_4\text{N}-\text{Au}-\}]_x^{2+}$ (**9**, $n = 3$; **10**, $n = 4$). The sine wave conformation of **9** (above). Selected bond parameters: Au(1)—P(1) 2.231(6) Å; Au(2)—P(2) 2.242(6) Å; Au(1)—N(1) 2.08(2) Å; Au(2)—N(2) 2.07(2) Å; N(1)—Au(1)—P(1) 178.0(5)°; N(2)—Au(2)—P(2) 176.6(6)°. The stretched polymer **10** (below). Selected bond parameters: Au—P(1) 2.234(2) Å; Au—N(1) 2.102(5) Å; N(1)—AuP(1) 168.3(1)°.

different. Thus, **9** has the *syn* conformation of the two gold(I) substituents with respect to the bridging diphosphine ligand, leading to a similar U-shape of each $(\text{CH}_2)_3(\text{PPh}_2\text{Au})_2$ unit as found in the ring compounds **8** and **1** but with no significant intra- or intermolecular $\text{Au}\cdots\text{Au}$ bonding interactions, the closest approach being 5.984 Å. Under these circumstances, ring formation is not favored and the polymer forms instead.

However, the U-shaped repeat units give the polymer a unique conformation which resembles a sine wave. Thus the bis(4-pyridyl)ethylene ligands on neighboring gold(I) centers fold back roughly parallel to one another, with the result that a “sinusoidal” rather than the expected linear or helical conformation is preferred. In complex **10**, the two gold(I) substituents have the *anti* conformation with respect to the diphosphine ligand; thus, the polymer has a more “stretched” linear structure. These compounds **9** and **10** are the first coordination polymers containing linear gold(I) centers to be structurally characterized, and given their interesting structures, it is likely that gold-containing polymers will constitute a rich research area.¹³ The strategy for synthesis of crystalline gold(I) polymers is clearly established by this work, but the conformations of individual polymers are expected to vary widely. New conformations of the polymer chains, and different forms of packing of the polymer chains, can be expected. For the compounds $[\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2-\text{Au}-\text{NC}_5\text{H}_4\text{CH}=\text{CHC}_5\text{H}_4\text{N}-\text{Au}-\}]_x^{2+}$, the ring structure with $x = 2$ is preferred when $n = 1$ or 2, but the polymer structure with $x = \infty$ is favored when $n = 3$ or 4.

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Supporting Information Available: Tables of crystal data, positional parameters, bond distances and angles, anisotropic displacement parameters, hydrogen atom coordinates for **8–10** and a view of the structure of **8** (15 pages). See any current masthead page for ordering and Internet access instructions.

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(12) Crystal data. For **8**: $\text{C}_{76}\text{H}_{68}\text{Au}_4\text{N}_4\text{P}_4(\text{CF}_3\text{CO}_2)_4$, MW = 2401.10, monoclinic, space group $C2/m$; $a = 37.934(6)$ Å, $b = 15.812(3)$ Å, $c = 10.133(1)$ Å; $\beta = 91.468(9)^\circ$; $V = 6075(14)$ Å³, $Z = 2$, $R_1 = 0.128$. (The intramolecular $\text{Au}\cdots\text{Au}$ distance is 3.625(3) Å; the crystal decayed during data collection, and though the structure is clearly defined, bond parameters are not accurately determined.) For **9**: $\text{C}_{39}\text{H}_{36}\text{Au}_2\text{N}_2\text{P}_2(\text{CF}_3\text{CO}_2)_2\cdot\text{CH}_3\text{OH}$, M = 1246.65; monoclinic, space group $P2_1/c$; $a = 21.474(3)$ Å, $b = 14.163(2)$ Å, $c = 17.112(2)$ Å; $\beta = 98.3(1)^\circ$; $V = 5149.6(1)$ Å³, $Z = 4$; $R = 0.0814$, $wR_2 = 0.1939$. (The shortest $\text{Au}\cdots\text{O}$ (trifluoroacetate) contact is 3.19 Å.) For **10**: $\text{C}_{40}\text{H}_{38}\text{Au}_2\text{N}_2\text{P}_2(\text{CF}_3\text{CO}_2)_2$, MW = 1228.64; $P-1$, $a = 8.8985(9)$ Å, $b = 9.590(1)$ Å, $c = 13.771(1)$ Å; $\alpha = 104.474(1)^\circ$, $\beta = 106.781(2)^\circ$, $\gamma = 100.062^\circ$; $V = 1050.0(2)$ Å³, $Z = 1$; $R = 0.0262$, $R_w = 0.0633$. (The shortest $\text{Au}\cdots\text{O}$ (trifluoroacetate) contact is 2.91 Å.)

(13) Note that a coordination polymer with trigonal planar gold(I) centers has been characterized and that several simple gold(I) compounds, such as AuCl , have polymeric structures. Hor, T. S. A.; Houlton, A.; Mingos, D. M. P.; Murphy, D. M.; Phang, L. T.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1993**, 3629–3630.