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Strongly Luminescent Three-Coordinate Gold(I) Polymers: 1D Chain-Link Fence and 2D Chickenwire Structures

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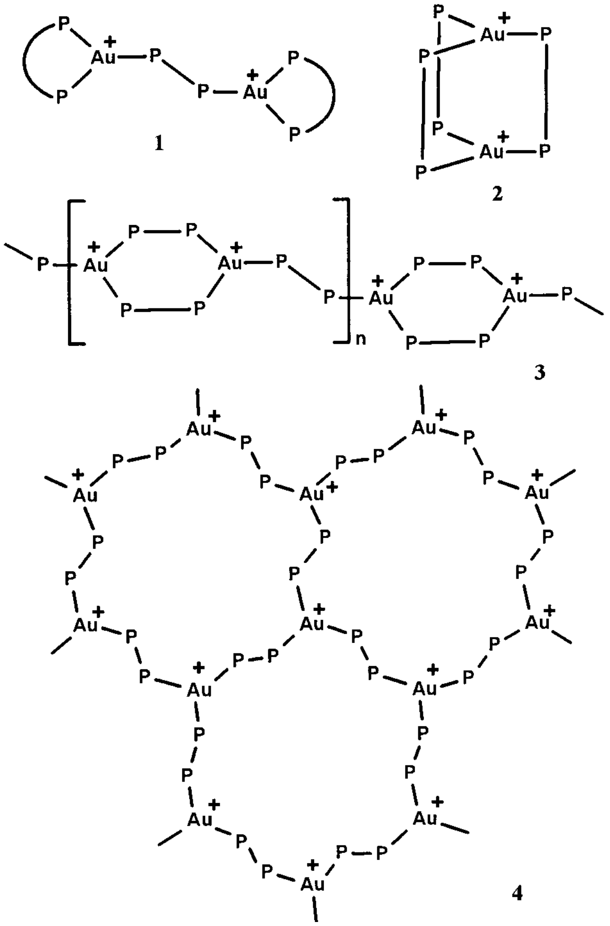
Since many gold(I) complexes exhibit room-temperature luminescence[1] and since metal-containing polymers are of interest as functional new materials,[2] there has been interest in the synthesis and photophysical properties of polymeric gold(I) complexes.[3] However, rigid-rod polymers containing 2-coordinate gold(I) centers are only weakly luminescent, although the red-shift compared to model complexes does indicate conjugation through the gold centers.[3] Since many 3-coordinate gold(I) complexes are strongly luminescent,[4] it was of interest to prepare 3-coordinate gold(I) polymers, and this article describes the first such polymers containing only phosphorus-donor ligands.[3] They have novel structures and are the first σ-bonded gold(I) polymers to exhibit strong room-temperature luminescence in the solid state.

With monodentate phosphine ligands, gold(I) can form complexes $[AuL_2]^+$, $[AuL_3]^+$, or $[AuL_4]^+$ but mononuclear gold(I) complexes with simple diphosphine ligands, of the type $[Au(LL)_2]^+$, are only known with 4-coordinate gold(I).[4] Binuclear complexes with 2- or 3-coordinate gold(I) centers of the types $[Au_2(LL)_2]^{2+}$ or $[Au_2(LL)_3]^{2+}$ are known, and the 3-coordinate gold(I) complexes may have structures **1**, with LL = $Cy_2PCH_2CH_2PCy_2$ or $[Fe(C_5H_4PPh_2)_2]$, or **2**, with LL = $Me_2PCH_2PMe_2$ or 2,6-C_6H_3N-$(PPh_2)_2$ (Chart 1).[4,5] No polymeric complexes are known. Working on the hypothesis that diphosphines which cannot chelate or which have a preference for the *anti* conformation of the phosphorus donors might give polymeric structures, the complexes with *trans*-$Ph_2PCH{=}CHPPh_2$ and $Ph_2P(CH_2)_4PPh_2$ were prepared.

Chart 1. Isomers of Empirical Formula $[Au(PP)_{1.5}]^+$, PP = Diphosphine



Complex **3** (Chart 1, LL = *trans*-$Ph_2PCH{=}CHPPh_2$), as the trifluoroacetate salt, was prepared by reaction of Cl−Au-LL-Au−Cl with CF_3CO_2Ag in the presence of free diphosphine LL.[6,7] The structure is shown in Figure 1 and can be described as a one-dimensional (1D) “chain-link fence” polymer. Each gold(I) center has distorted trigonal planar stereochemistry with $[AuP_3]^+$ coordination. Each 10-membered $Au_2(\mu$-$LL)_2$ ring is then connected to the neighboring ring through the two gold atoms by further μ-LL groups to give an infinite chain structure. The ^{31}P NMR spectrum of this complex contained two singlet resonances at δ = 40.8 and 24.9 in a roughly 2:1 ratio, tentatively assigned to phosphorus atoms in and outside the rings, respectively. However, no PP coupling was observed, and it is possible that ligand exchange at the labile gold(I) centers occurs.

Complex **4** (Chart 1, LL = $Ph_2P(CH_2)_4PPh_2$) was prepared in a similar way but was crystallized, following anion exchange, as the dicyanoaurate(I) salt.[6,7] The structure shown in Figure 2 is remarkable. It contains fused $Au_6(\mu$-$LL)_6$ rings, with each gold present as a distorted trigonal planar $[AuP_3]^+$ center and with all gold atoms crystallographically equivalent; each gold atom is then involved in three such rings as shown fully for the central gold atom in structure **4** (Chart 1 and Figure 2). The result is an infinite graphite-like or “chickenwire” two-dimensional (2D) sheet structure, but with very large 42-membered rings. The six gold atoms of each ring are in an extended chair conformation, and there is

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(6) Synthetic procedures are given in the Supporting Information.

(7) Selected data for complex **3**. NMR (CD_2Cl_2, 400 MHz): $\delta(^{31}P)$ = 40.8 [s, *P*-Au, ring], 24.9 [s, *P*-Au, “link”-diphosphine]. Crystal data: $Au(Ph_2PCH{=}CHPPh_2)_{1.5}(CF_3CO_2)]$. CH_3OH, $C_{42}H_{37}AuF_3O_3P_3$, fw = 936.59, monoclinic, *C*2/*c*, $a = 21.7919(4)$, $b = 13.5308(3)$, $c = 26.4892(6)$ Å, $\beta = 99.693(1)°$, $V = 7699.1(3)$ Å^3, $Z = 8$, $d_{calcd} = 1.616$ Mg/m^3, T = 200(2) K, $\mu = 3.999$ mm^{-1}, $R_1 = 0.0414$, $wR_2 = 0.1058$. Selected data for complex **4**. NMR (CD_2Cl_2/MeOD, 400 MHz): $\delta(^{31}P)$ = 34.7 [s, *P*-Au−P, simple ring], 35.6 [s, *P*-Au−P_2, 3-coordinate gold], 42.1 [s, *P*-Au−CN]. Crystal data for **4**: $Au(Ph_2PCH_2CH_2CH_2CH_2PPh_2)_{1.5}$. $Au(CN)_2.2CH_3OH$, $C_{46}H_{50}Au_2N_2O_2P_3$, fw = 1149.72, triclinic, *P*-1, $a = 14.1027(7)$ Å, $b = 14.2985(7)$Å, $c = 14.3500(9)$Å, $\alpha = 63.154(2)°$, $\beta = 63.508(2)°$, $\gamma = 88.398(3)°$, $V = 2255.5(2)$ Å^3, $Z = 2$, $d_{calcd} = 1.693$ Mg/m^3, $T = 150(2)$ K, $\mu = 6.641$ mm^{-1}, $R_1 = 0.0544$, $wR_2 = 0.1186$.

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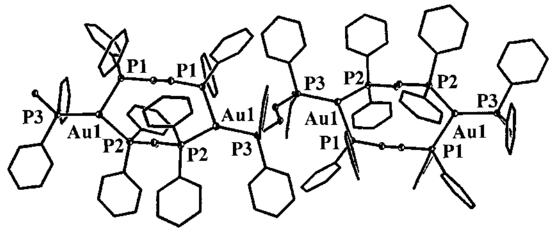

Figure 1. A view of part of the "chain-link fence" structure of the polymeric cation **3**. Thermal ellipsoids of phenyl carbon atoms are not shown for clarity. Selected distances and angles: Au1−P1 = 2.394(1); Au1−P2 = 2.393(1); Au1−P3 = 2.336(1) Å; P1−Au1−P2 = 105.10(4); P1−Au1−P3 = 122.89(4); P2−Au1−P3 = 127.00(4)°.

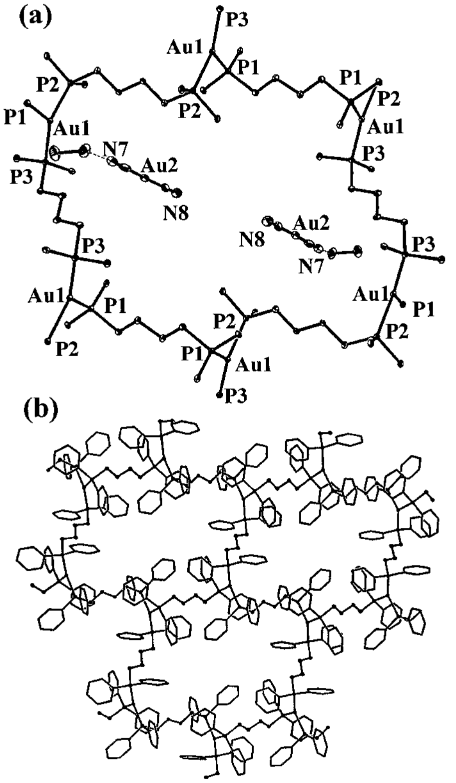

Figure 2. A view of part of the "chickenwire" structure of the polymeric cation **4**. (a) A single 42-membered ring, with two occluded $[Au(CN)_2]^{-}\cdot\cdot$ HOMe groups, showing only the *ipso*-carbon atoms of the phenyl groups. Selected distances and angles: Au1−P1 = 2.381(2); Au1−P2 = 2.394(2); Au1−P3 = 2.334(2) Å; P1−Au1−P2 = 102.42(7); P1−Au1−P3 = 129.00(7); P2−Au1−P3 = 127.59(7)°. (b) Three rings, containing the connecting gold atom at the center of the structure, illustrating the propagation of the 2D polymeric structure.

a center of symmetry at the ring center. The cavities within and between the rings are occupied by two $[Au(CN)_2]^{-}$ ions and four molecules of methanol, two of which are hydrogen-bonded to dicyanoaurate ions (O−H··N bonded, Figure 2a). The ^{31}P NMR spectrum of complex **4** is complex, and thus indicates that there is an equilibrium present in solution, probably containing smaller oligomeric fragments formed by partial ligand dissociation and by ligand exchange to yield some $[Au_2(CN)_2(\mu\text{-}Ph_2P(CH_2)_4PPh_2)]$.

The local stereochemistries of the 3-coordinate gold(I) centers in **3** and **4** are remarkably similar, each containing one shorter Au−P bond [Au1−P3 = 2.336(1) and 2.334(2) Å in **3** and **4**, respectively] and one smaller P−Au−P angle [P1−Au1−P2 = 105.10(4)° and 102.42(7)° in **3** and **4** respectively] (Figures 1 and 2). Steric effects preclude Au··Au bonding in both complexes. Perhaps reflecting the similar structures, the complexes **3** and **4** give similar strong blue-purple luminescence at room temperature in the solid state as pressed KBr disks, typical of trigonal gold(I) complexes.[8] The observation of strong luminescence, together with the similarity in the emissions of complexes **3** and **4**, suggests that there is very little extended conjugation present in these complexes. Conjugation is not possible through the saturated diphosphine in **4** but might occur through the unsaturated diphosphine in **3**. Apparently it does not occur to a significant extent, and therefore emission from essentially localized $[AuL_3]^{+}$ centers is observed for both polymeric complexes.

In summary, this article describes the first polymeric diphosphine gold(I) complexes having $[AuP_3]^{+}$ centers that lead to strong room-temperature luminescence. The polymers feature interesting 1D "chain-link fence" and 2D "chickenwire" structures. They are prepared very easily by self-assembly, and the structures observed can be rationalized on the basis of conformational preferences of the diphosphine ligands. In particular, the complexes **3** and **4** can be viewed as products of single or double ring-opening polymerization (ROP)[2] respectively of the binuclear **2** (Chart 1). The structure of **3** (Chart 1) follows naturally, but the double ROP could give rise to a number of structures, and the unique structure **4** could not have been predicted readily. The extent of the ROP depends on the degree of ring strain in the precursor **2** (or **3**) for the particular diphosphine ligand. These principles are clearly applicable to the synthesis by self-assembly of other coordination polymers.

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Supporting Information Available: Synthetic procedures and Tables of X-ray data for complexes **3** and **4** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[8] For comparison, $[Au(PPh_3)_3]^{+}$ has $\lambda_{em} = 481$ nm and $[Au_2(dcpe)_2(\mu\text{-}dcpe)]^{2+}$ has $\lambda_{em} = 501$ nm in the solid state.[4b,4c] In each case, the emission is attributed to a primarily metal-centred transition $a_2''(6p_z) \rightarrow e'(d_{x^2-y^2}, d_{xy})$.[3] The higher energy emission for **3** and **4**, which are broad and have $\lambda_{em} =$ ca. 420 nm, together with indications of vibrational coupling in the emission bands, may indicate a contribution from π^*(Ph) in the excited state in addition to $6p_z$(Au).[4b,4c]