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Synthesis and Structural Characterization of an Au–P Linked Chain Polymer. The Molecular Structure of Two Pseudo-polymorphic Forms of [{AuCl(μ-dppf)}$_n$] [dppf = 1,1′-bis(diphenylphosphino)ferrocene]

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A novel iron–gold 1,1′-bis(diphenylphosphino)ferrocene (dppf) complex [{AuCl(μ-dppf)}$_n$] contains a co-ordination polymer based on trigonal P_2AuCl linkages and has been structurally characterized in both polar and apolar pseudo-polymorphic forms.

The chemistry of gold(I) is dominated by the formation of linear molecular co-ordination compounds although there are a few examples of trigonal-planar and tetrahedral complexes particularly with phosphine ligands.[1] In the solid state the linear gold(I) complexes frequently show weak Au···Au intermolecular interactions which have been attributed to relativistic effects.[2] There are a few examples of polymeric gold(I) complexes, *e.g.* [{Au(PPh_2)}$_n$] and [{Au(C≡CPh)}$_n$], but they are generally insoluble and as a consequence poorly characterized.[3] More recently Puddephatt and co-workers[4] have reported on oligo- and poly-meric complexes of Au^I, but again solubility problems made unambiguous structural assignments difficult. In this communication we describe what we believe to be the first example of a polymeric gold(I) complex based on trigonal co-ordination about the gold centres.

When 1,1′-bis(diphenylphosphino)ferrocene (dppf) is added in a 1:1 ratio to [AuCl(SMe_2)] in CH_2Cl_2 the compound [{AuCl(μ-dppf)}$_n$] **1** is formed.* This yellow compound which is soluble in CH_2Cl_2 and $CHCl_3$ may be obtained in two crystalline modifications by the addition of hexane. The crystalline modifications may be separated manually as either rounded diamond-shape (**1a**) or rhombic prismatic (**1b**) forms. The molecular structures of both forms have been determined by single-crystal X-ray analysis.†

Both compounds **1a** and **1b** comprise (Figs. 1 and 2) polymeric-chain structures involving bridging ferrocenylphosphine units linking trigonal Au–Cl groups. For **1a** co-ordination around the Au is distorted trigonal with P–Au–Cl angles of 112.7(2) and 104.0(2)° and P–Au–P 143.0(2)°. The Au–Cl bond length of 2.624(9) Å and the Au–P bond lengths of 2.298(5) and 2.309(6) Å are typical of trigonal gold(I).[1] In contrast, **1b** (Fig. 2) exhibits more regular geometry with the P–Au–Cl angles of 112.7(1) and 110.8(1)° and P–Au–P of 136.5(1)°. The Au–P bond lengths are equal at 2.315(2) Å, though the Au–Cl distance [2.550(3) Å] is noticeably shorter than that in **1a**.

There are marked differences in the conformations of the two polymeric chains in **1a** and **1b**. These arise through combinations of torsional differences about Au–P, P–C_5H_4 and about the X(1)–X(2) vector in the ferrocenyl unit [where X(1) and X(2) are the centroids of the cyclopentadienyl rings]. The molecular torsion angle α, defined by P(1)–X(1)–X(2)–P(2), is $\approx$180° in **1b** and $\approx$130° for **1a**. The torsion angle defined by Cl–Au···Au–Cl is 179.2° in **1b** and 81.6° in **1a**. As a consequence of these conformational variations the Au···Au and Au···Fe separations differ from **1a** to **1b**. In **1a** the Au···Au distances are 8.55 Å and the Au···Fe distances are 4.14 and 4.43 Å, whereas in **1b** these distances are 8.36, 4.20 and 4.17 Å, respectively. Another notable difference between these two structural forms is that **1a** crystallizes in a polar space group, whereas **1b** is centrosymmetric. In both structures the polymeric chains are propagated *via* glide operators. In **1b** the resulting structure is approximately centrosymmetric with

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* Compound 1 was obtained in 90% yield when reactions were carried out with 0.2 g of the gold compound. (Found: C, 48.2; H, 3.4. $C_{34}H_{28}AuClFeP_2{\cdot}CH_2Cl_2$ requires C, 48.3; H, 3.3%). NMR ($CDCl_3$): ^1H, δ 7.45 (br s, 20 H), 4.56 (s, 4 H); ^{13}C, δ 134.6 (s), 133.1 (s), 130.5 (s), 129.5 (d, J = 52.4 Hz), 76.5 (s), 75.2 (s), 75.1 (d); ^{31}P, δ 40.96. Fast atom bombardment mass spectrum: m/z 948 [Au_2(fdpp)], 752 (M + H − Cl).

† *Crystal data.* **1a**: $C_{34}H_{28}AuClFeP_2{\cdot}0.4CH_2Cl_2$, crystal dimensions 0.059 × 0.117 × 0.284 mm, $M = 820.7$, orthorhombic, $F2dd$, $a = 11.096(4)$, $b = 31.507(10)$, $c = 39.71(3)$ Å, $U = 13\,882(11)$ Å^3, $Z = 16$, $F(000) = 6413$, $D_c = 1.571$ g cm^{-3}, μ(Cu-Kα) = 134.9 cm^{-1}. Data were measured on a Siemens P3/PC diffractometer with graphite-monochromated Cu-Kα radiation using ω scans. The structure was solved by direct methods and refined anisotropically using absorption corrected data to give $R = 0.0492$, $R' = 0.0489$, $w^{-1} = \sigma^2(F) + 0.0005F^2$, for 2152 independent observed reflections $[|F_o| > 4\sigma(|F_o|)]$.[5]

1b: $C_{34}H_{28}AuClFeP_2{\cdot}2.85X$ (X represents unidentified partial occupancy solvent fragments allowed for as carbon atoms), crystal dimensions 0.100 × 0.133 × 0.666 mm, $M = 821.0$, monoclinic, $P2_1/c$, $a = 12.917(6)$, $b = 18.321(6)$, $c = 16.242(4)$ Å, $\beta = 110.11(2)°$, $U = 3610(2)$ Å^3, $Z = 4$, $F(000) = 1604$, $D_c = 1.511$ g cm^{-3}, μ(Mo-Kα) = 46.5 cm^{-1}. Data were measured on a Siemens P4/PC diffractometer with graphite-monochromated Mo-Kα radiation using ω scans. The structure was solved by the direct methods and refined anisotropically using absorption corrected data to give $R = 0.0421$, $R' = 0.0404$, $w^{-1} = \sigma^2(F) + 0.0006F^2$, for 4516 independent observed reflections $[|F_o| > 4\sigma(|F_o|)]$.[5] Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

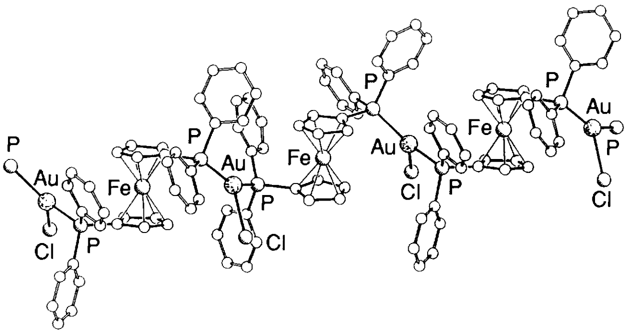

Fig. 1 Part of the polymeric (dppf)AuCl(dppf)AuCl chain in the polar crystals **1a**

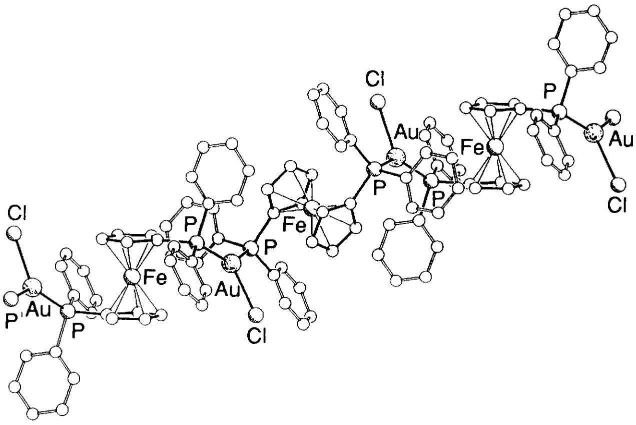

Fig. 2 Part of the polymeric chains of **1b** showing the essentially *anti* relationship of adjacent Au–Cl bonds

respect to the Fe centres, with adjacent Au–Cl bonds *anti*, whilst in **1a** they all lie on one side of the chain * (see above).

Previous structural studies on fdpp with gold(I) have revealed linear and trigonal geometries. The linearly co-ordinated gold in $[(AuCl)_2(dppf)]$ is involved in intermolecular Au $\cdots$ Au interactions between molecules.[6] The two independent molecules have P–X(1)–X(2)–P torsion angles of 180 and ≈150°. The trigold complex $[(AuCl)_3\{Fe(\eta\text{-}C_5H_4PPh_2)[\eta\text{-}C_5H_3PPh_2\text{-}CH(Me)N(Me)CH_2CH_2NMe_2]\}]$ contains two linear terminal PAuCl groups, and a central trigonal bridging P_2AuCl unit.[7] The geometry around this grouping more closely resembles **1b** than **1a**, with P–Au–P and P–Au–Cl angles of 134(2) and 113(2)°, and Au–P and Au–Cl bond lengths of 2.31(2) and 2.52(3) Å, respectively. The torsion angle P–X(1)–X(2)–P for the two ferrocenyl moieties is 178°.

Polymerization represents a useful strategy for ensuring strong intermetallic spin interactions and has been exploited with notable effect in the design of molecular-based magnetic materials.[8] Preliminary studies on **1** indicate that oxidation of the ferrocenyl moiety is possible,† thus producing unpaired iron-based spins in the polymeric chains. Intrachain Fe $\cdots$ Fe distances for **1a** and **1b** are 8.351 Å and 8.123 Å, sufficiently close for magnetic interactions to occur. The shortest interchain Fe $\cdots$ Fe distance is 11.419 Å in **1a** and 11.031 Å in **1b**.

The demonstrated ability to form polymeric gold chains using multidentate phosphines opens up the possibility for the use of these ligands as building blocks for gold-based polymeric and macromolecular structures. The solubility of these polymers in organic solvents is a particularly attractive feature as far as their characterization is concerned. Molecular weight determinations have indicated that the polymer breaks down in solution to give lower molecular weight oligomers.

Acknowledgements

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* The polarity effect in **1a** is particularly large with $R^+ = 0.0492$, and $R^- = 0.1854$.

† ESR spectroscopy gave evidence for the formation of the $S = \frac{1}{2}$ ferrocenium cation in a chlorine oxidized sample of **1**.