Construction of a Knitted Crystalline Polymer through the Use of Gold(I)–Gold(I) Interactions

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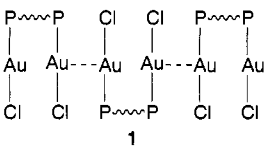
Crystals of $(AuI)_2\{\mu$-bis(diphenylphosphino)hexane$\}$ form polymeric chains (through Au–Au contacts), which are interwoven to produce discrete layers that lie between cleavage planes of the crystal.

The production of extended solid state structures (with the potential for novel optical, electronic, magnetic and mechanical properties) from small molecular or ionic components represents a new challenge to chemical synthesis. Self-assembly techniques are an effective means to take advantage of weak interactions between molecules to create a more complex superstructure. Intermolecular interactions that have been used to produce such superstructures include hydrogen bonding,[1] weak metal ion coordination,[2] and shaped van der Waals forces.[3] Here, we describe a new woven layered structure, which uses the attractive interaction between two gold(I) ions to connect the molecular components. This attractive interaction has been estimated to be comparable in energy to a hydrogen bond[4] and to result in contact between two gold(I) ions of less than 3.5 Å.[5]

A survey of the Cambridge Crystallographic Data Base[6] augmented with data from this laboratory indicates that Au^I–Au^I contacts are present in 16% of the 25 examples of compounds of the type $(R_3P)AuX$ where X is a halide ligand. However, when a diphosphine ligand is used, the occurrence of these Au^I–Au^I contacts increases. Of the 23 examples, 26% display intramolecular interactions and a remarkable 61% display intermolecular interactions. Those in the latter category generally form chains, **1**.[7] The formation of discrete dimers, **2**, is less common with only two examples found.[8] The polymeric compounds, **1**, can have the chains running parallel or crisscrossing one another. However, with $(AuI)_2(\mu$-dpph) we have observed the formation of an unprecedented woven layered structure the complexity of which exceeds that seen in other solids of type **1**.

Colourless crystals of $(AuCl)_2(\mu$-dpph) [dpph is bis(diphenylphosphino)hexane] were prepared by mixing (Me_2S)-AuCl with dpph in CH_2Cl_2 and precipitation of the complex by the addition of diethyl ether. These were subsequently converted into $(AuI)_2(\mu$-dpph) by treatment with tri(butyl)(propyl)ammonium iodide in MeOH. The results of X-ray diffraction studies of $(AuCl)_2(\mu$-dpph), crystallized from CH_2Cl_2/diethyl ether, and $(AuI)_2(\mu$-dpph), crystallized from CH_2Cl_2/methanol, are shown in Fig. 1–3.† Fig. 1 shows the basic molecular structure of the individual dinuclear complexes. In each case the hexane chain adopts a staggered conformation and is fully elongated. The P–Au–X groups are nearly linear. While both P–Au–Cl groups in $(AuCl)_2(\mu$-dpph) jut out almost perpendicularly to the line of methylene groups, only one of the P–Au–I groups in $(AuI)_2(\mu$-dpph) adopts a similar orientation. The other is positioned so that it extends approximately in the direction of the methylene chain. The intermolecular interactions in the two compounds differ markedly. In $(AuI)_2(\mu$-dpph), Au(1) in one molecule interacts with Au(2) in the next. The Au(1)–Au(2) distance is 3.124(2) Å. However in $(AuCl)_2(\mu$-dpph) there is no comparable Au–Au interaction. The shortest Au···Au distance is 5.726 Å, and the solid merely contains isolated, centrosymmetric molecules.



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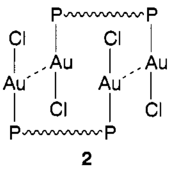

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The Au–Au interactions in $(AuI)_2(\mu$-dpph) produce chains of type **1**. Fig. 2 shows a drawing of one such chain. Notice that the chain has a pronounced sinusoidal shape. This shape is correlated with the interweaving of the chains. Fig. 3 shows a schematic drawing that displays the nature of the woven layers. In Fig. 3 the circles represent the gold atoms, the long lines that connect the gold atoms represent the individual molecules of $(AuI)_2(\mu$-dpph), and the shorter lines are the Au(I)–Au(I) contacts. Fig. 4 shows a more detailed drawing of the chains from a different perspective. Organization of a linear polymer into such a complex knitted structure is only feasible through the use of self-assembly techniques with weak interactions between molecular components.

The layered structure of $(AuI)_2(\mu$-dpph) is reflected in its mechanical properties. Pressure applied to a razor blade aligned along the *ab* plane of a single crystal of $(AuI)_2(\mu$-dpph) results in smooth cleavage. In contrast with the blade placed along the *ac* plane a greater pressure is required to break the crystal, and shattering, rather than cleavage, occurs. These observations correlate with the solid state structure, since as seen in Fig. 4, there are only weak van der Waals contacts along the *ab* planes that separate the woven layers.

The observation that $(AuI)_2(\mu$-dpph) forms a polymeric solid with significant Au^I–Au^I interactions whereas these are absent in $(AuCl)_2(\mu$-dpph) is consistent with both calculations of Pyykkö *et al.*[9] which show that these interactions are strengthened as the ligand is changed from chloride to bromide and then to iodide, and with experimental results on related complexes of $\{(Me_2PhP)AuX\}_n$.[10]

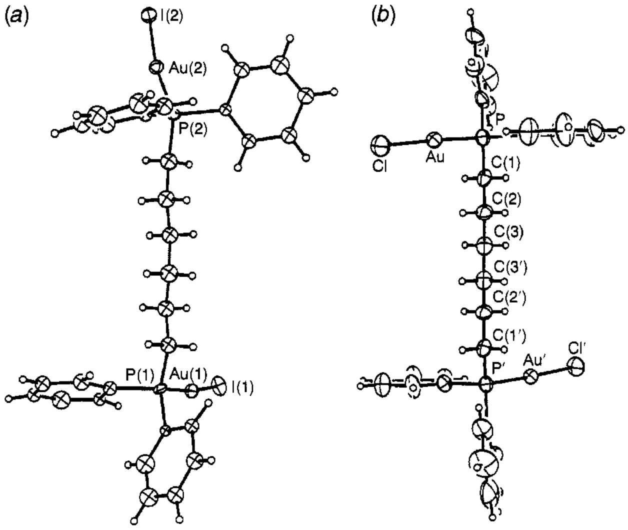

Fig. 1 Perspective views of individual molecules of (*a*), $(AuI)_2(\mu$-dpph); and (*b*) $(AuCl)_2(\mu$-dpph) with 50% thermal contours for all atoms

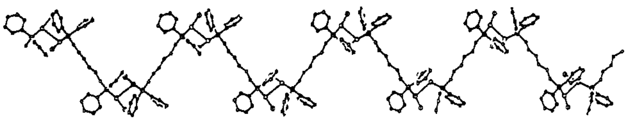

Fig. 2 A drawing of a chain of molecules of $(AuI)_2(\mu$-dpph)

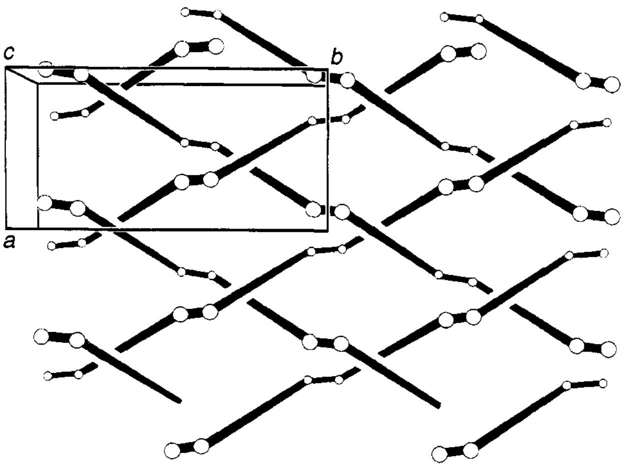

Fig. 3 A drawing of a layer of the woven structure of $(AuI)_2(\mu\text{-dpph})$ with the positions of the gold atoms shown as open circles. The short lines are the gold–gold contacts, while the longer wedges connected the two gold atoms within a single molecule of $(AuI)_2(\mu\text{-dpph})$.

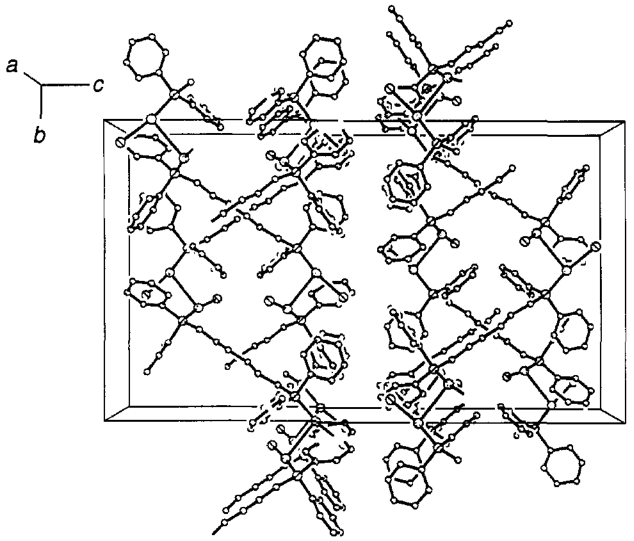

Fig. 4 A view of the unit cell of $(AuI)_2(\mu\text{-dpph})$ that shows two layers and emphasizes the *ab* cleavage plane

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Footnote

† *Crystal data*: colourless plates of $C_{15}H_{16}AuIP$ that were obtained by diffusion of MeOH into a CH_2Cl_2 solution of the compound form in the orthorhombic space group *Pbcn* with a = 9.707(2), b = 19.301(5), c = 33.032(7) Å, at 200 K with Z = 8 with the use of graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation. Refinement of 3015 reflections with $F > 4.0\,\sigma(F)$ and 175 parameters yielded R_1 = 0.075. The largest peak in the final difference map (2.3 e Å^3) is 0.913 Å from Au(2) and results from Fourier ripples from that heavy atom.

Colourless plates of $C_{15}H_{16}AuClP$ that were obtained by diffusion of diethyl ether into a CH_2Cl_2 solution of the compound form in the monoclinic space group *C*2/*c* with a = 10.642(4), b = 14.588(4), c = 19.903(4) Å, β = 93.10(2)° at 200 K with Z = 4 with the use of graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation. Refinement of 2942 reflections with $F > 4.0\,\sigma(F)$ and 163 parameters yielded R_1 = 0.061 and Rw = 0.060. Atomic coordinates, bond lengths and angles, and thermal parameters for both structures have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1. The largest peak in the final difference map (4.0 e Å^3) is 0.847 Å from the gold atom and results from Fourier ripples from that heavy atom.

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