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# Coordination polymers of gold(I) with dithiolate and diphosphine ligands

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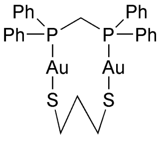
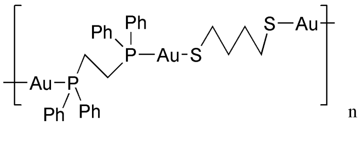
*Received (in Cambridge, UK) 22nd May 2002, Accepted 25th June 2002*
*First published as an Advance Article on the web 22nd July 2002*

**The first neutral, hybrid organic–inorganic coordination polymers with linear gold(I) centres in the backbone have the formula [X(OCH$_2$CH$_2$O$_2$CCH$_2$SAu)$_2$(μ-dppee)]$_n$, X = 1,4-C$_6$H$_4$ or C$_{10}$H$_6$, dppee = *trans*-bis(diphenylphospino-)ethylene, are easily formed by self-assembly during crystallization from macrocyclic isomers ($n$ = 1), and form sheet structures anchored by secondary Au···S and S···S interactions in the solid state.**

Coordination polymers and gold(I) thiolates are each topics of considerable interest in their own right.[1–8] Thus, the incorporation of metal centres into polymer chains can lead to interesting catalytic, electrical, optical, or magnetic properties of the materials,[1] while the interest in gold(I) thiolates arises from their use in gold pastes, self-assembled monolayers, chemical vapour deposition and pharmacology.[5] Diphosphine gold(I) complexes also have interesting biological activity and the photoluminescent properties of many gold(I) phosphine and thiolate complexes suggest potential applications in optical, chemosensing or other nanoscale devices.[2] Furthermore, intermolecular Au···Au bonding in gold(I) compounds can be used in the formation of supramolecular architectures, including cross-linking of polymer chains, induction of chain folding or formation of liquid crystals.[3–7] Several ionic gold(I) polymers, including the important caesium salt of gold(I) thiomalate used in chrysotherapy, have been structurally characterized, but the known neutral organic–inorganic polymers containing linear gold(I) centres have usually proved to be too insoluble to crystallize.[5–7] For example, gold(I) with most combinations of dithiolate and diphosphine ligands gives cyclic derivatives such as **A**, while longer chain dithiolates give insoluble compounds such as **B** whose detailed structures are unknown.[8] This article reports the first structure determination of polymers of type **B** and shows that the polymers undergo supramolecular association in the solid state.



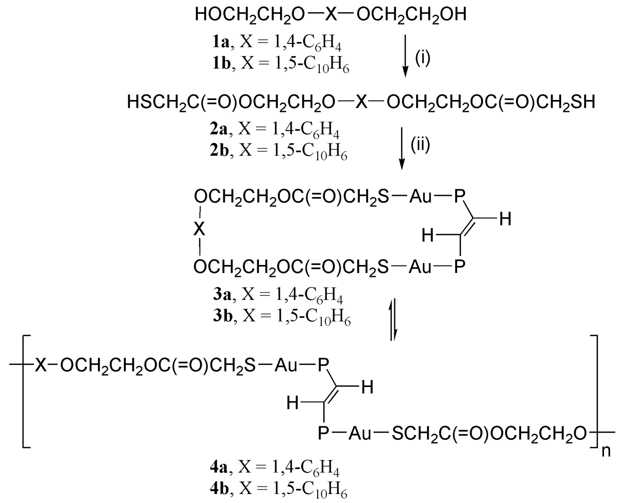
**A**



**B**

The new chemistry is shown in Scheme 1. The dithiol reagents **2** were prepared from the corresponding diols **1**.[9] The digold(I) thiolate complexes were then prepared by reaction of **2** with [(μ-dppee)(AuO$_2$CCF$_3$)$_2$], dppee = *trans*-Ph$_2$PCH=CHPPh$_2$, prepared *in situ* from [(μ-dppee)(AuCl)$_2$] and silver trifluoracetate followed by filtration to remove AgCl. The gold thiolate complexes were isolated as colourless, stable solids. The complexes were soluble in dichloromethane or nitrobenzene, and the $^1$H and $^{31}$P NMR spectra gave sharp resonances, with well resolved couplings when expected, consistent with formation of the ring structures **3** rather than the polymers **4** (Scheme 1), and the ring structures were confirmed by ESI-MS.† Complex **3b**, like other phosphine(thiolato)gold(I) complexes, exhibits room temperature luminescence ($\lambda_{em}$ = 468 nm with excitation at 375 nm) in dichloromethane solution.[2,8]

Although the digold(I) complexes are present as macrocycles **3** in solution, in the crystalline solid form they exist as polymers **4**. The complexes **4a** and **4b** have very similar structures as shown in Fig. 1, and they crystallize in the same space group (*P*2/*n*).† In each case the compounds exist as stretched one-dimensional polymers, with nearly linear stereochemistry about gold(I) (P–Au–S = 178.0(1) and 178.9(1)° in **4a** and **4b**, respectively). There is a crystallographic centre of symmetry at the midpoint of the diphosphine C=C bond in each case, and so the P–Au vectors are aligned at exactly 180° to each other, giving a perfect *anti* conformation. The centroid of the linking



**Scheme 1** Reagents: (i) HSCH$_2$CO$_2$H, TsOH; (ii) [(Au(O$_2$CCF$_3$)$_2$(-(μ-dppee)], −CF$_3$CO$_2$H.

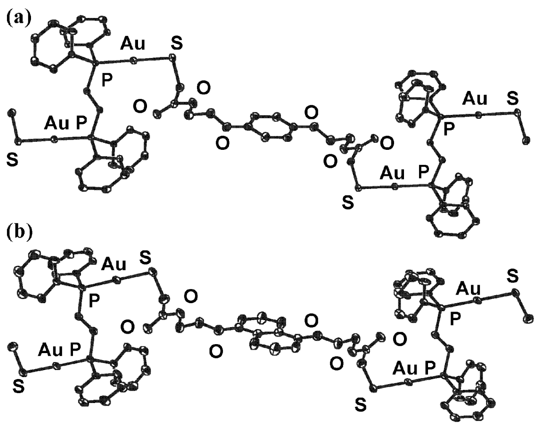


**Fig. 1** Views of the structures of the polymers (a) **4a** and (b) **4b**. Selected distances for **4a**, Au–S 2.296(3), Au–P 2.256(2) Å; **4b**, Au–S 2.300(3), Au–P 2.257(3) Å. The polymer pitch is 20.987 and 21.737 Å for **4a** and **4b**, respectively.

DOI: 10.1039/b204992a

benzene or napthalene ring of the dithiolate in **4a** or **4b**, respectively, also occupies a crystallographic special position, and so the Au–S vectors in each chain are also oriented at 180 to each other. There is local helicity in the flexible organic connecting groups (Fig. 1 and 2), but the inversion centres preclude the presence of chain chirality.

The crystal packing of the linear polymers is similar for both complexes and is illustrated in Fig. 2 in the case of complex **4a**. Within each layer, the chains lie parallel to one another and there are no very close contacts (Fig. 2a). However, the chains that lie in neighbouring layers lie crosswise, as illustrated in Fig. 2b, in an orientation that leads to close head-to-tail, interlayer contacts of individual Au–S groups, as shown in Fig. 2, giving a slightly twisted parallelogram local structure (the dihedral angle $S\cdots Au–S\cdots Au = -10.3°$ in **4a**). The weak secondary interactions, indicated by dashed lines in Fig. 2, are $Au\cdots S = 3.69$ and 3.53 Å, and $S\cdots S = 3.60$ and 3.61 Å in **4a** and **4b**, respectively.[10] The transannular gold distances of 4.95 and 4.72 Å in **4a** and **4b** are too long to represent a strong aurophilic attraction. The $Au_2S_2$ parallelogram structure has been observed in molecular gold(I) thiocyanate complexes, but the relative distances $S\cdots S$ and $Au\cdots Au$ vary considerably, perhaps indicating that overall secondary binding strength (sum of $Au\cdots S$, $S\cdots S$ and $Au\cdots Au$) can be maintained as the Au–S groups slide with respect to one another.[10] There are also secondary aryl–aryl attractions; for example, in **4b**, edge to face π-stacking exists between the phenyl phosphine groups and the naphthalene ring (centroid$\cdots$centroid 5.308 Å, interplanar angle 79.7°, edge to face distance 4.24 Å).[11] In both complexes, voids between the polymer chains are occupied by solvent molecules, dichloroethane in **4a** and dichloromethane in **4b**.

This work shows that there is an easy equilibrium between the macrocycles **3** and polymers **4**, with **3** favoured in solution by the entropy factor and **4** in the solid state by additional secondary bonding forces and by the relief of ring strain. This is maximised with the dppee ligands by the strong preference for the *anti*-configuration of the diphosphine ligand. Gold(I) is a labile metal centre and allows easy equilibration between the different structural forms, and the present work establishes that polymeric dithiolate diphosphine complexes of gold(I) can be crystallized given an appropriate choice of ligands. It is likely that the chains form to a significant extent only during crystallization; the easy equilibration is essential for success and might allow deposition of polymeric coatings.

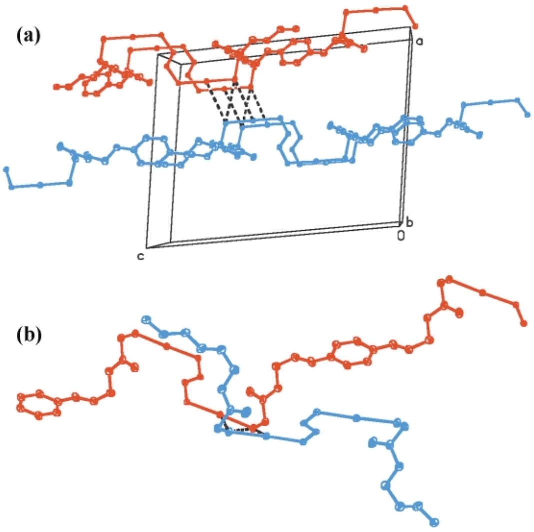


**Fig. 2** Views of the supramolecular association between chains of **4a** (phenyl groups of the diphosphine ligands are omitted for clarity). (a) Parallel chains in a layer (blue) with secondary bonding to a neighbouring layer (red) through $Au_2S_2$ parallelograms, and (b) a roughly perpendicular view showing two crossing chains from neighbouring layers.

We thank the NSERC (Canada) for financial support and a scholarship to WH. R. J. P. thanks the Government of Canada for a Canada Research Chair.

## Notes and references

† Experimental, spectroscopic and X-ray data: complex **4b** was prepared by reaction of $[(AuCl)_2(\mu\text{-dppee})]$ (0.300 g, 0.348 mmol) in $CH_2Cl_2$ (10 mL) with silver trifluoroacetate (0.161 g, 0.697 mmol) in MeOH (2 mL), followed by filtration to remove AgCl, and then addition of dithiol **2b** (0.138 g, 0.348 mmol) in $CH_2Cl_2$ (2 mL). The solution was stirred for 3 h, then the product was precipitated by addition of petroleum ether (bp = 40–60 °C) (100 mL), collected by filtration and washed with acetone and ether (Yield: 0.361 g, 88%). NMR for **3b** in $CDCl_3$: $\delta(^1H)$ 7.30–7.50 [m, 20H, Ph]; 7.67, 7.05, 6.45 [m, 6H, $C_{10}H_6$]; 7.10 [t, 2H, $^2J(PH) = 19$ Hz, CH=CH]; 4.32 [s, 4H, $CH_2CO_2$]; 4.06 [s, 4H, $OCH_2$]; 3.53 [s, 4H, $CH_2S$]; $(^{31}P)$ 34.97 (s). ESI-MS($CHCl_3$-MeOH–MeCN): Calc. for **3b** + $H^+$, $m/z = 1185.1151$. Found, 1185.1154. NMR data for **3a**: $\delta(^1H)$ 7.40–7.62 [m, 20H, Ph]; 7.39 [t, 2H, $^2J(HP) = 18$ Hz, $C_6H_4$]; 4.23 [t, 4H, $^2J(HH) = 5$ Hz, $CH_2CO_2$]; 3.93 [t, 4H, $^2J(HH) = 5$ Hz, $ArOCH_2$]; 3.58 [s, 4H, $CH_2S$]; $\delta(^{31}P)$ 35.68 (s). ESI-MS: Calc. for **3a** + $H^+$, $m/z = 1135.0995$. Found, 1135.0995. X-Ray data: $\lambda = 0.71073$ Å, monoclinic, $P2/n$, $Z = 2$; **4a**·$2C_2H_4Cl_2$, $C_{44}H_{38}Au_2Cl_4O_6P_2S_2$, $M = 1324.24$, $T = 294(2)$ K, $a = 14.8337(8)$, $b = 8.3956(4)$, $c = 19.235(1)$ Å, $\beta = 98.642(3)°$, $V = 2368.3(2)$ Å$^3$, $D_c = 1.857$ Mg m$^{-3}$; $\mu = 6.614$ mm$^{-1}$, $F(000) = 1276$, $R_1 = 0.0548$, $wR_2 = 0.1285$; **4b**·$CH_2Cl_2$, $C_{45}H_{42}Au_2Cl_2O_6P_2S_2$, $M = 1269.68$, $T = 200(2)$ K, $a = 16.070(1)$, $b = 8.5562(3)$, $c = 19.983(1)$ Å, $\beta = 105.700(2)°$, $V = 2645.1(3)$ Å$^3$, $D_c = 1.594$ Mg m$^{-3}$; $\mu = 5.820$ mm$^{-1}$, $F(000) = 1228$, $R_1 = 0.0635$, $wR_2 = 0.1666$. CCDC 177622 and 177623. See http://www.rsc.org/suppdata/cc/b2/b204992a/ for crystallographic data in CIF or other electronic format.

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