$[Tl(OPPh_3)_2][Au(C_6F_5)_2]$: the first extended unsupported gold–thallium linear chain

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$Li[Au(C_6F_5)_2]$ reacts with $TlNO_3$ in the presence of $OPPh_3$ affording a complex of stoichiometry $[AuTl(C_6F_5)_2(OPPh_3)_2]_n$, which presents different luminescence properties depending on the conditions and whose crystal structure reveals the existence of unsupported Au–Tl bonds forming a polymeric linear chain.

There is a renewed interest in mixed gold–transition metal compounds because of their fascinating and unique chemical and physical properties. A central issue in their chemistry is the study of closed-shell metal–metal interactions, which have been attributed to correlation effects that are strengthened by the relativistic effects for gold.[1] Structural and theoretical evidence has been accumulated for an entire family of cation–cation interactions between d^8–d^{10}–s^2 systems.[2] Particularly interesting are extended linear chain compounds, because the rationalization of the bonding of these structures still remains as a challenge.[3,4] For instance, $Tl_2Pt(CN)_4$,[5] with a Tl–Pt distance of 3.14 Å, was expected to be ionic with some covalent character[6] although correlation effects and the crystal-field contributions seem to be also important.[7] In contrast, $[AuTl\{Ph_2P(S)CH_2\}_2]$,[3,8] with a shorter Tl–Au distance (3.003 Å), displays mainly ionic bonds between Tl^+ and $[AuX_2]^-$ moieties.[2] This latter unit is also present in the polymeric species $[AgAuX_2L_2]$,[9,10] where X is a pentafluorophenyl group, thus avoiding any bridging effect. Mössbauer spectroscopic studies of such species indicate that $[Au(C_6F_5)_2]^-$ groups act as Lewis bases; the presence of perfluorophenyl groups seems to be the key for their donor properties,[11] which are similar to those postulated for dinuclear units of the form $[Au(ylide)]_2$.[12–14]

Despite the results previously reported, $[Au(C_6F_5)_2]^-$ has not hitherto been employed in the synthesis of other heterometallic compounds. We report here the synthesis and characterization of $[Tl(OPPh_3)_2][Au(C_6F_5)_2]$ (**1**), the first extended unsupported gold–thallium linear chain. This material is formed by reacting a mixture of triphenylphosphine oxide and a solution of $TlNO_3$ in MeOH with a freshly prepared solution of $Li[Au(C_6F_5)_2]$ in diethyl ether at −78 °C. The $LiNO_3$ formed is filtered off and the colourless solution is layered with pentane. Yellow-green crystals of complex **1** are collected after three days in a 40% yield. Compound **1** shows analytical and spectroscopic data in accordance with the proposed structure† and behaves as a 1 : 1 electrolyte in acetone. The absence of colour in ether or acetone solution implies that the interactions between the metal centres are restricted to the solid state.

In contrast, when the same reaction is carried out with the NBu_4^+ instead of the lithium salt, the complex is not formed and the gold(I) starting material is recovered unaltered. However, treatment of $[Au(C_6F_5)_2Cl(PPh_3)]$ with equimolecular amounts of thallium acetylacetonate surprisingly affords complex **1**. The mechanism of such a reaction is not clear, but it involves the reduction of the gold(III) centre and the oxidation of the triphenylphosphine.

The structure of **1** was determined by single-crystal X-ray diffraction[15]‡ (Fig. 1). The two independent gold atoms lie on inversion centres and thus display exact linear co-ordination by the C_6F_5 groups with Au–C distances of 2.058(5), 2.053(6) Å, whereas the thallium centre is bonded to two $OPPh_3$ ligands [O(1)–Tl–O(2) = 80.61(3)°] with typical Tl–O distances of 2.483(3) and 2.550(4) Å. The compound forms a one-dimensional polymer parallel to the crystallographic x axis. Including the metal–metal interactions, the geometry at gold is almost square planar and that at thallium is distorted trigonal bipyramidal with a vacant equatorial co-ordination site, presumably associated with the stereochemically active lone pair. The Tl–Au distances [Au(1)–Tl = 3.0358(8), Au(2)–Tl = 3.0862(8) Å] are nearly equal and similar to the sum of thallium and gold metallic radii (3.034 Å). They are similar to those found in $[AuTl(Ph_2P(S)CH_2)_2]_n$ [Tl–Au(intramolecular) = 2.959(2), Tl–Au(intermolecular) = 3.003(2) Å],[3,8] where two ‘supporting’, $Ph_2P(S)CH_2$ ligands are C-bonded to each gold centre and S-bonded to each thallium atom of a linear chain in which the metallic centres exhibit similar geometries as in **1**. Complex **1** may be considered as containing $[Au(C_6F_5)_2]^-$ and

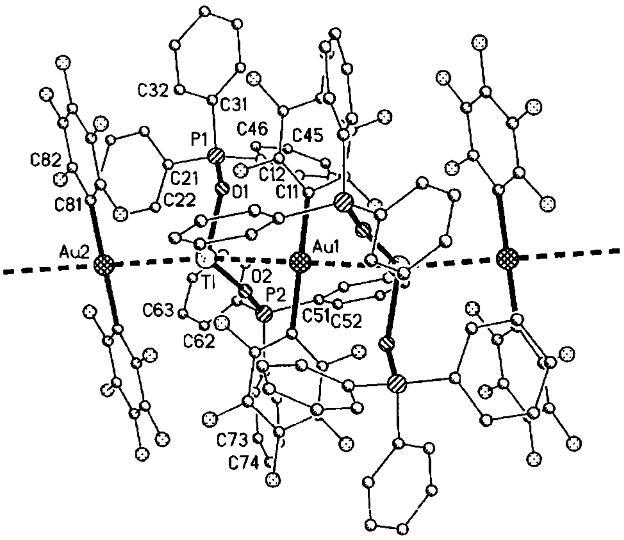

Fig. 1 Molecular structure of complex **1**. Selected distances (Å) and angles (°): Au(1)–C 2.058(5), Au(2)–C 2.053(6), Au(1)–Tl 3.0358(8), Au(2)–Tl 3.0862(8), Tl–O(1) 2.483(3), Tl–O(2) 2.550(4), C(11)–Au(1)–Tl 90.8(2), C(11)^{i}–Au(1)–Tl 89.2(2), C(81)–Au(2)–Tl^{ii} 88.0(2), C(81)–Au(2)–Tl 92.0(2), O–Tl–O 80.61(13), O(1)–Tl–Au(1) 94.73(11), O(2)–Tl–Au(1) 86.16(11), O(1)–Tl–Au(2) 99.04(11), O(2)–Tl–Au(2) 105.55(11), Au(1)–Tl–Au(2) 163.163(8). Symmetry operators: i $-x, -y+1, -z$; ii $-x+1, -y+1, -z$.

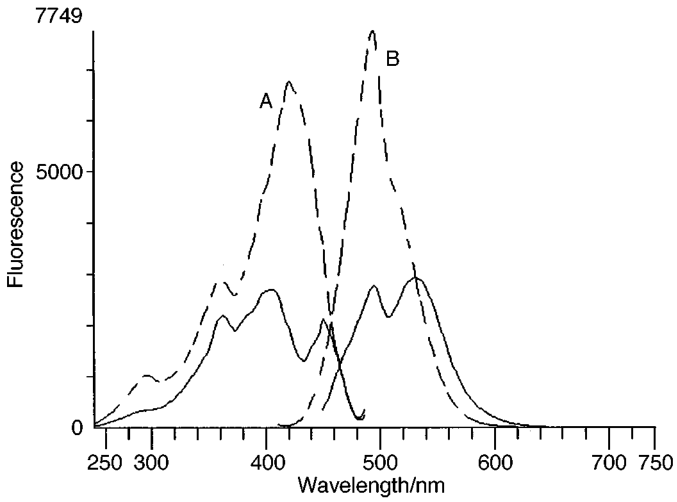

Fig. 2 Excitation and emission spectra of complex **1** in the solid state at 293 K (dashed line) and at 77 K (solid line) (excitation in curve **A**, emission in curve **B**)

$[Tl(OPPh_3)_2]^+$ ions, which are linked by weak M–M′ bonds thus forming the first unsupported Au–Tl linear chain. Four weak Tl···F contacts (3.313–3.488 Å) may also contribute to the stability of the system.

Furthermore, the heteronuclear complexes $[AuTl(Ph_2P(S)CH_2)_2]$ and $[Au_2Pb(Ph_2P(S)CH_2)_4]$[3,8] with d^{10} and s^2 electronic configurations are luminescent and also form linear Au–M linear chains. Similarly, complex **1** luminesces both at room temperature (293 K) (excitation at 421 nm, emission at 494 nm) and at 77 K (maximum excitation at 403 nm, emission at 494 and 530 nm) in the solid state (Fig. 2). The excitation and emission spectra for **1** are virtually mirror images of each other with only a small separation between excitation and emission peaks, suggesting that the dominant emission in this complex is perhaps fluorescence.

Previous Fenske–Hall molecular orbital calculations for a gold–thallium complex[3,8] indicated that although no formal metal–metal single bond is present, the HOMO is a σ* orbital mainly of Tl(I) and the LUMO is a σ orbital of both Au(I) and Tl(I) orbitals. Thus, a feature of this excited state is that the transfer of an electron from an antibonding orbital to a bonding orbital results in a net increase of intermetallic bonding in the excited state, but the luminescence spectrum suggests that there is no change in the Au–Tl distances in this linear chain species.

Neither the gold(I) nor Tl(I) precursor complexes are luminescent under similar conditions suggesting that the emission is a result of interactions between the metals. Moreover, when the product is dissolved in non-halogen solvents the green colour of the solid disappears and the resultant colourless solution is non-emissive. Evaporation of the solvents regenerates the colour and its optical properties. Another interesting feature is when **1** is saturated with halogenated solvents and irradiated with UV light, the emission is also quenched but, upon evaporation of the solvent, it does not regenerate the green product, but instead an uncharacterized grey solid appears which shows an emission at higher energy (476 nm). If the process of dissolution in CH_2Cl_2 is carried out in the dark, the green product is recovered without any change. This promising result seems to indicate that under UV radiation the excited state is able to react with halocarbons in an electron transfer reaction, perhaps making this product appropriate for practical applications.

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Notes and References

† Selected data for **1**: (Calc. for $C_{48}H_{30}AuF_{10}O_2P_2Tl$: C, 44.51; H, 2.33. Found: C, 44.14; H, 2.00%). IR: ν(P=O): 1178 (vs); C_6F_5: 1503 (vs), 957 (vs), 784 (m) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.0 (s, $OPPh_3$); ^{19}F NMR ($CDCl_3$): δ −115.4 (m, F_o), −158.6 (t, *J* 20 Hz, F_p), −161.8 (m, F_m). MS (FAB+): *m*/*z*(%) = 761(5) $[M]^+$; MS (ES): *m*/*z*(%) = 531(100) $[M]^-$. Λ (5.0×10^{-4} M, acetone): 113 Ω^{-1} cm^2 mol^{-1}.

‡ *Crystal data* for **1**: $C_{48}H_{30}AuF_{10}O_2P_2Tl$, T = −100 °C, M = 1292.00, monoclinic, space group $P2_1/n$, a = 12.112(3), b = 27.006(3), c = 13.515(2) Å, β = 91.891(12)°, V = 4418.2(14) Å^3, Z = 4, μ = 7.11 mm^{-1}, 10486 reflections (Siemens P4 diffractometer, Mo-Kα radiation, $2\theta_{max}$ 50°, ω-scans), 7764 unique. Refinement on F^2 using all reflections; program system SHELXL-93. Final R = 0.0305, R_w = 0.0456, for 581 parameters and 544 restraints; max. $\Delta\rho$ 0.6 e Å^{-3}. CCDC 182/1021.

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