

[[AuTl(C₆Cl₅)₂(toluene)]₂(dioxane)]: A striking structure that leads to a blue luminescence†

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Received (in Cambridge, UK) 30th April 2003, Accepted 30th May 2003

First published as an Advance Article on the web 18th June 2003

The complex [[AuTl(C₆Cl₅)₂(toluene)]₂(dioxane)] displays a structure with the thallium(I) center in an unprecedented trigonal planar environment, showing the shortest Au–Tl interaction ever found, a toluene molecule in a η⁶-mode and the “disappearance” of the Tl(I) inert pair, usually stereochemically active. These characteristics are responsible for its unusual luminescent behaviour.

Heterometal complexes displaying metal–metal interactions without the presence of auxiliary bridging ligands are usually built using several strategies that include hydrogen bonding, π-stacking or, more recently, by means of what is called metallophilic attraction, a specific feature of closed-shell metals consisting of oligomerization not accomplished by conventional covalent or coordinative bonding. The most documented example among these attractions is *Aurophilicity*, and, thus, this phenomenon has been observed in a variety of mononuclear and polynuclear gold(I) species and has been described in recent experimental and theoretical reviews.¹ In this sense, while aurophilic attractions can be considered the upper extreme of metallophilic interactions in strength with values that can even reach 46 kJ mol⁻¹, Tl(I)⋯Tl(I) interactions are among the weaker ones, being estimated below 20 kJmol⁻¹.² Recent theoretical studies of these interactions conclude that, while aurophilic attractions are enhanced by relativistic effects, these effects weaken the inherent van der Waals attractions of the interactions between s² metal centres.³ By contrast, Au(I)⋯Tl(I) interactions generated by acid–base reactions provide an additional electrostatic force and thus, metallophilicity between gold(I) and thallium(I) centres in extended linear chains with an average metal–metal separation of 3.03 Å is estimated at about 276 kJmol⁻¹, of which 80% is due to ionic interaction and 20% to dispersion attraction.⁴ This result is striking since these interactions appear between centres in +1 oxidation state, and these centres would normally be expected to repel each other. In contrast, they produce aggregates with intermetallic separations shorter than the sum of their van der Waals radii (3.62 Å). Consequently, the rationalization of the bonding in these species is still a challenge. In addition, many of these complexes form highly luminescent extended arrangements in solid state with potential applications as LEDs or selective VOCs sensors.⁵

This work is part of our current interest in the chemistry of heteronuclear gold–thallium systems made up by reaction of pentahalophenyl gold(I) derivatives of the type Q[AuR₂] (R = C₆F₅, C₆Cl₅) with Tl(I) salts.^{4–6} The crystal structures of these complexes involve a large variety of assemblies, as discrete molecules,⁶ extended linear chains^{4,5,6} or two- or three-dimensional networks⁶ with different coordination numbers and geometries at thallium.

Here we describe the synthesis, structure and optical properties of the tetranuclear complex [[AuTl(C₆Cl₅)₂(toluene)]₂(dioxane)] (**1**), which displays an unprecedented

metal–metal interaction which is considered responsible for its luminescent behaviour. This white solid is obtained in high yield by reacting a suspension of [AuTl(C₆Cl₅)₂]_n⁵ in toluene with dioxane. Its analytical and spectroscopic data are in accordance with the proposed stoichiometry.⁷

Single crystals of **1** suitable for X-ray diffraction studies were obtained by slow diffusion of hexane in a saturated solution of the complex in toluene, allowing its crystal structure, which shows very interesting characteristics, to be unequivocally established.† This structure consists of tetranuclear units containing two [Au(C₆Cl₅)₂]⁻ units, two Tl⁺ centres and a dioxane molecule linked *via* unsupported Au⋯Tl and Tl⋯O interactions with a toluene molecule interacting with each thallium centre in a η⁶-mode (Figure 1). The complex contains an inversion centre in the middle of the dioxane making each half molecule of **1** equivalent. The first striking feature is the Au–Tl distance of 2.8935(3) Å, which is the shortest one described to date,^{4–6,8} being even shorter than the sum of Au–Tl covalent radii (3.08 Å⁹ or 2.92 Å¹⁰), indicating the unprecedented strength of this interaction. The solvent molecule is only weakly coordinated with a Tl–O distance of 2.827(4) Å, longer than the Tl–O (THF) distances observed in other Tl complexes (2.74(3)–2.781(7) Å),^{4,6,11} but shorter than the Tl–O (acetone) distances observed in [Au₂Tl₂(C₆Cl₅)₄](CH₃)₂C=O (2.903(9) and 2.968(9) Å).⁶ The coordination sphere of the Tl atoms is completed by an unusual η⁶-like π-arene contact to a toluene molecule resulting in an nearly trigonal-planar environment for each thallium centre (considering the third position occupied by the centroid of the phenyl ring of the toluene) with a sum of angles around the Tl atom of 355.2°. This implies that, very surprisingly, the stereoactivity of the inert pair, usually stereochemically active,¹² is not apparent in this case. This fact, together with the short Au–Tl distance makes us wonder about the nature of this interaction. The Tl–C distances range from

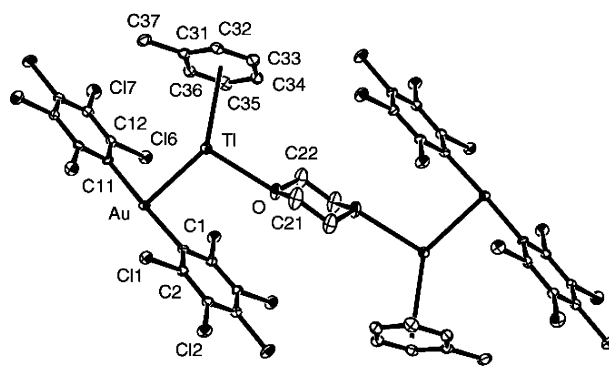


Fig. 1 Crystal structure of complex **1**. The thermal ellipsoids are drawn at the 30% level; hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Au–Tl 2.8935(3), Au–C1 2.055(5), Au–C11 2.052(5), Tl–O 2.827(4), Tl–C31 3.411(5), Tl–C32 3.462(6), Tl–C33 3.455(6), Tl–C34 3.378(6), Tl–C35 3.291(6), Tl–C36 3.319(6), E(=plane)1(C31–C36)–Tl 3.079(3), Au–Tl–O 105.5(1), Ct(centroid)1(C31–36)–Tl–Au 139.6, Ct1–Tl–O 110.1.

† This work is dedicated to the memory of Dr M^a Teresa Pinillos.

3.291(6) to 3.462(6) Å, slightly longer than some of the Tl–C distances observed in the few examples of η^6 -like π -arene thallium complexes described to date that range from 3.14 to 3.49 Å.^{12,13}

In addition to its striking structure, complex **1** also shows a very interesting luminescent behaviour in solid state at room temperature and at 77 K (Figure 2). Its excitation spectrum shows a maximum at *ca.* 340 nm, associated with a maximum blue emission band appearing at 442 nm at room temperature and at 468 nm at 77 K. It is worth noting that although blue luminescent materials are one of the components necessary for full-colour displays, they are still scarce and, for instance, in organometallic compounds, usually require appropriate choice of substituents in organic emitters.¹⁴ Blue photoluminescence from d¹⁰ metal complexes has also been observed in dinuclear derivatives.¹⁵ The fluorescence lifetime, determined by the phase-modulation technique in solid state at room temperature fits a double-exponential decay with values of 1843.98 and 752.08 ± 0.05 ns ($\chi^2 = 0.327$). This lifetime measurement within the microsecond time scale seems to indicate that the emission is probably phosphorescence. In this context, similar values were found in the gold–thallium complex [Au₂Tl₂(C₆Cl₅)₄](CH₃)₂C=O, in which the excited state was almost completely based on the thallium centres, in agreement with the TD-DFT calculations carried out.⁶ Similarly, in complex **1**, the TD-DFT results also agree with this proposal and, thus, the thallium centres are likely to be the responsible emitter atoms for the luminescence in this case. On the other hand, and in reference to this and our previous work, the [Au(C₆Cl₅)₂][−] units are likely to be in the origin of the electronic transitions. In short, this transition can be considered as a MMCT (Metal (gold) to Metal (thallium) Charge Transfer) in origin. Interestingly, the blue emission contrasts with those previously described for extended linear chains in the sense that the reduced Au–Tl distance found in **1** should produce a shift of the emission to lower energies if compared to those. In fact, previous Fenske–Hall molecular orbital calculations^{8a} indicate that a reduced Au–Tl distance would produce a better overlapping of the 5d_{z²}(Au) and 6s(Tl) orbitals reducing the HOMO–LUMO gap and, consequently, the energy of the emission. By contrast, in this case, complex **1** displays an unprecedented blue emission for these Au–Tl systems. This result is likely to be originated by the characteristics of this interaction.

Finally, complex **1** loses its emissive properties in solution, where the Au–Tl interaction is probably no longer present. In addition, the electronic absorption spectra in acetone for **1** and for the gold(I) precursor NBu₄[Au(C₆Cl₅)₂] show similar features with very low absorptions in the 385–324 nm spectral

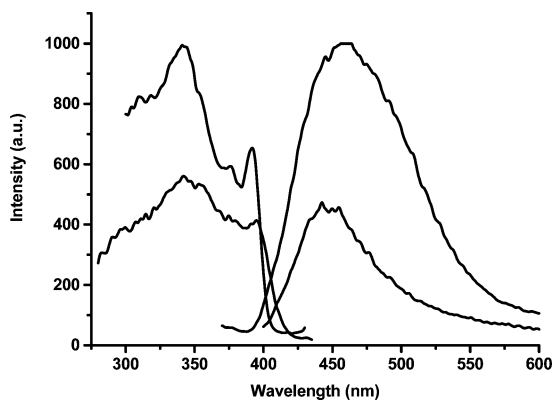


Fig. 2 Excitation and emission spectra of complex **1** in the solid state at 293K (upper lines) and at 77K (lower lines).

range, which are assigned to transitions localized in the π -orbitals of the perhalophenyl groups modified by the presence of the gold centre.⁶ The initial optical properties of **1** are recovered by evaporation of the solvent.

In short, this complex does not show the stereochemically active inert pair and displays the shortest Au–Tl distance and the higher emission reported for this kind of system, results that are likely to be due to an unusually strong interaction between the metal centres, which is currently under study.

This work was supported by the UR (API02/12), C.A.R. (ANGI2001/28) and DGI (MCYT) (BQU2001-2409)

Notes and references

‡ Crystal data for **1**: C₂₁H₁₂AuCl₁₀OTl, *M* = 1036.14, crystal dimensions 0.2 × 0.2 × 0.1 mm, triclinic, P $\bar{1}$, *a* = 9.3482(1), *b* = 11.1221(1), *c* = 13.1833(2) Å, α = 78.009(1), β = 89.278(1)°, γ = 81.670(1), *V* = 1326.42(3) Å³, *T* = −100 °C, *Z* = 2, μ (MoK α) = 12.615 mm^{−1}, 19605 measured reflections, 6281 independent reflections (*R*_{int} = 0.040), 309 refined parameters with *R*1 = 0.0363 and *wR*2 = 0.1055 for *I* > 2 σ (*I*), Goodness-of-fit on *F*² = 1.057. CCDC 204510. See <http://www.rsc.org/suppdata/cc/b3/b304835g/> for crystallographic data in CIF or other electronic format.

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- Complex **1** was prepared in high yield by adding 0.2 mmol (18 μ L) of dioxane to a suspension of [AuTl(C₆Cl₅)₂]_n (0.2 mmol, 0.18 g) in toluene (20 mL). The suspension was stirred for 15 minutes, and the solvent was evaporated to *ca.* 5 mL. Addition of *n*-hexane led the precipitation of **1** as a white solid. Yield: 0.15 g (75%). ¹H NMR (300 MHz, [D₈]THF, 25 °C, TMS): δ 7.3 (m, 10H; CH), 3.5 (s, 8H; CH₂), 2.30 ppm (s, 6H; CH₃); MS: (ES[−]): *m/z* (%): 695 (100) [Au(C₆Cl₅)₂][−]; (ES⁺): 204 (100) Tl⁺; elemental analysis calcd for C₄₂H₂₄Au₂Cl₂₀O₂Tl₂ (%): C 24.34, H 1.17; found: C 24.75, H 0.79.
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