

[Au₂Tl₂(C₆Cl₅)₄](CH₃)₂C=O: A Luminescent Loosely Bound Butterfly Cluster with a Tl(I)–Tl(I) Interaction

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In the last years the attractions between closed-shell species have provoked theoretical controversy and experimental evidence of such attractions has largely been observed.¹ Thus, many compounds of this type have been described as species displaying gold(I)–gold(I) interactions (*Aurophilicity*)² or heterometallic assemblies with a large variety of structural dispositions, such as discrete molecules, extended linear chains of mono-,³ di-,⁴ tri⁵ or tetra-nuclear⁶ units or even sheets or three-dimensional networks.⁷ Nevertheless, as far as we know no unsupported butterfly disposition built through interactions between closed-shell metal ions has been reported, although this is a very common structural arrangement in clusters with formal metal–metal bonds.

In this paper we report the synthesis of a loosely bound butterfly cluster of alternating gold and thallium centers in which the thallium atoms are in an unusually low coordination mode. In addition, the interacting thallium centers are likely to be responsible for the optical properties in solid state and even in solution.

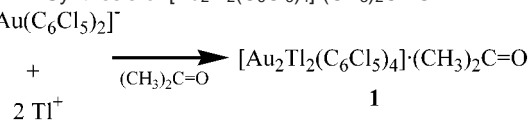
The synthetic strategies to synthesize unsupported gold-heterometal complexes are mainly two: *a*) encapsulation of heterometal ions by trigonal gold(I) complexes (metallocryptands)⁸ and *b*) reactions between acid heterometal complexes and basic gold precursors which lead to supramolecular assemblies formed via acid–basic stacking.^{3,5,6}

Together with these comments and using the latter strategy, we recently reported the synthesis of Au(I)–Ag(I) and Au(I)–Tl(I) based molecules by reaction of gold(I) complexes of the type Q[AuR₂] (Q = Li, NBu₄; R = C₆F₅, C₆Cl₅) with silver(I) or thallium(I) salts. In the former the reaction gave rise to a polymeric chain of tetranuclear gold–silver units linked by short gold–gold interactions.⁶ In the latter the presence of ligands such as phosphine oxides³ or amines⁷ led to either a polymeric chain or to two- or three-dimensional structures depending on the ligand and on the perhalophenyl group attached to gold.

We have now extended these results to study the reaction between the gold(I) and thallium(I) precursors in the absence of ligands different than the solvent.

The yellow complex [Au₂Tl₂(C₆Cl₅)₄](CH₃)₂C=O (**1**) was readily prepared by reaction of an acetone solution containing 1 equivalent of colorless [NBu₄][Au(C₆Cl₅)₂] with 1 equivalent of TlPF₆ (Scheme 1).⁹ The IR spectrum shows the absorptions due to the C₆Cl₅ groups bonded to the gold(I) atom at 618 and 840 cm⁻¹ as well as a strong absorption at 1677 cm⁻¹ assigned to the stretching ν(C=O) vibration in the acetone molecule which is shifted to low energy if compared with the free molecule (1716 cm⁻¹).

Scheme 1. Synthesis of [Au₂Tl₂(C₆Cl₅)₄](CH₃)₂C=O **1**



The crystal structure¹⁰ of complex **1** is shown in Figure 1. It consists of a tetranuclear unit where the metals are held together through four unsupported Au–Tl interactions and an additional Tl–Tl interaction resulting in a loosely bound butterfly cluster. The Au–Tl distances are within the range 3.0331(6)–3.1887(6) Å, the shortest ones similar to the sum of thallium and gold metallic radii (3.034 Å)¹¹ and to those observed, for example, in the extended unsupported Au–Tl linear chain [Tl(OPPh₃)₂][Au(C₆F₅)₂]³ (3.0358(8) and 3.0868(8) Å). The thallium atoms are in close proximity showing a Tl–Tl interaction with a distance of 3.6027(6) Å, similar to the intramolecular Tl–Tl distances observed in [TlS₂CNET₂]₂¹² (3.60 and 3.62 Å), but longer than some of the distances found in Tl[C(SiMe₃)₃]¹³ (3.322(1)–3.638(1) Å) or in some amide derivatives¹⁴ within the range from 3.403(3)–3.837(3) Å. In this context, it is worth noting that the closest metal–metal distances in α-thallium are 3.408 and 3.457 Å.¹⁵ The gold centers are almost linearly coordinated with the pentachlorophenyl groups with Au–C distances within the range 2.058(10)–2.073(9) Å. The thallium atoms show weak interactions with the oxygen atom of an acetone

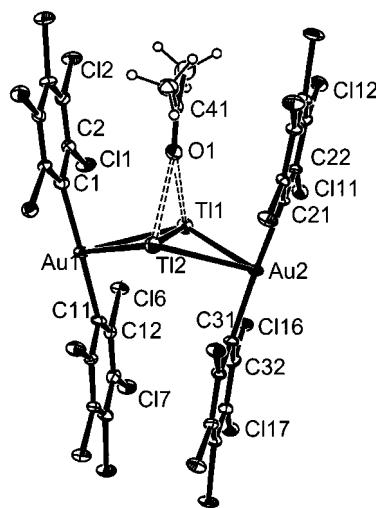


Figure 1. Molecular structure of complex **1**. Selected distances (Å): Au(1)–Tl(1) 3.033(6), Au(1)–Tl(2) 3.188(6), Au(2)–Tl(1) 3.1164(6), Au(2)–Tl(2) 3.0733(5), Tl(1)–Tl(2) 3.6027(6), Au(1)–C(1) 2.058(10), Au(1)–C(11) 2.062(9), Au(2)–C(21) 2.061(9), Au(2)–C(31) 2.073(9), Tl(1)–O(1) 2.968(9), Tl(2)–O(1) 2.903(9).

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molecule displaying Tl–O distances of 2.968(9) and 2.903(9) Å. These distances are longer than those found in $\{trans,trans,trans-[PtTl_2(C_6F_5)_2(C\equiv C^iBu)_2](acetone)_2\}_n$ ¹⁶ where the acetone molecules are very weakly bonded to thallium (2.83(2) Å) and clearly longer than the sum of the covalent radii (2.21 Å) or the Tl–O distance observed in $[Tl(OPPh_3)_2][Au(C_6F_5)_2]^3$ (2.483(3) and 2.550(4) Å). Finally, each metallic center shows four metal–chlorine contacts within the range 3.284(3)–3.406(3) Å for gold or 3.297(3)–3.492(3) Å for thallium that contribute to the stabilization of the structure.

Complex **1** luminesces both at room temperature (exc. at 400 nm, em. at 556 nm) and at 77K (exc. at 420 nm, em. at 556 nm) in solid state showing an interesting independence of the temperature, probably due to the environmental rigidity. Neither the gold(I) nor the thallium(I) precursor complexes are luminescent at similar energies suggesting that the emission is a result of the interactions between the metals. The lifetime measurement within the microsecond time scale ($\tau_1 = 2 \mu s$; $\tau_2 = 0.7 \mu s$) seems to indicate that the emission is probably phosphorescence. In this context, it is worth noting that the other pentahalophenyl gold–thallium chains also show luminescence, but shorter lifetimes and a strong dependence on the temperature.^{3,7}

In addition, and very interestingly, the luminescent behavior observed for this complex in solution also differs from that of the previously reported gold–thallium chains and it is closer to that of the metallocryptands reported by Catalano keeping the structure in solution.⁸ Thus, while the extended linear chains lose their emissive properties in solution at room temperature, complex **1** is luminescent and shows a solvent dependence on the emission. For instance, acetone, tetrahydrofuran and acetonitrile solutions of **1** shows emission bands at 566 nm (exc. 356 nm), ($\tau = 427$ ns), 528 nm (exc. 358 nm), ($\tau = 236$ ns) and 539 nm (exc. 346 nm), ($\tau = 173$ ns), respectively. These values are close in energy to the emission observed in the solid state, suggesting that the same excited state is found both in solution as in the solid state. The longer value of the lifetime in acetone solution is indicative of a more lasting emitting excited state of the molecule in the presence of this donor solvent.

In this context, TD-DFT calculations carried out for the simplified model system $[Au_2Tl_2(C_6H_5)_4]$ (see Supporting Information) show that the orbital from which the emission is produced is almost completely based on both thallium atoms. These results seem to indicate that the dinuclear thallium(I) unit present in solid state is likely to be responsible for this luminescence, which in the case of the solution is perturbed by the presence of solvent molecules with donor capabilities. Unfortunately, complex **1** is not soluble in the most common noncoordinating solvents such as toluene, benzene, chloroform, etc. that would allow us to confirm this fact.

In the gas phase, under mass spectrometry conditions (FAB +) (Fast Atom Bombardment), a peak at $m/z = 1103$ (25%) assigned to $[AuTl_2(C_6Cl_5)_2]^+$ is detected.

Finally, despite the structural similarity of this tetranuclear unit with the gold–silver system reported by us,⁶ an increase in the concentration of the sample does not produce shifts in the excitation or emission bands, implying that the aggregation process in fluid solution through gold–gold interactions is not produced in this complex and that those interactions are not responsible for the optical properties.

On the other hand, equivalent conductivity measurements of this complex in acetonitrile over the 10^{-4} – 10^{-3} mol/L range show a value of $A = 1100$ from the Onsager equation ($\Lambda_e = \Lambda_o - Ac^{1/2}$) ($\Lambda_o = 127$; $R^2 = 0.992$) characteristic of a 2:1 electrolyte.^{17,18} This result again differs from the polymeric chains reported,^{3,4} which show equivalent conductivity measurements typical of 1:1 electro-

lytes. The interpretation of these results based on luminescence and conductivity measurements suggest a thallium–thallium interaction exists in solution which is probably stabilized by solvent molecules. Theoretical calculations previously reported on the Tl_2H_2 compound at a SCF–CI level led to the conclusion that attractive interactions between the molecules through metal–metal contacts are weak; lower than $20 \text{ kJ}\cdot\text{mol}^{-1}$.¹⁹ Abundant evidence exists for attractions between monovalent thallium atoms like, for instance, those in the $[(C_5(CH_2C_6H_5)_5)Tl]_2$ dimer;²⁰ nevertheless, as far as we know, this kind of interaction in solution has not been reported.

Future ligand variations and theoretical studies of the systematically modified butterfly core could be useful to assign the excited-state properties, as well as to know the nature of the Tl(I)–Tl(I) interactions in these systems.

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Supporting Information Available: X-ray crystallographic files for **1** (CIF). Details of the packing of the molecular units in the cell, intermolecular distances, luminescence spectra of **1** and TD-DFT results (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (9) Anal. Calcd (found) for $Au_2Tl_2C_{27}H_6Cl_{20}O$: C, 17.5 (17.9); H, 0.3 (0.4). ¹H NMR (300 MHz, DMSO-*d*₆, 25 °C, TMS): $\delta = 2.08$ (s, 6H; CH₃).
- (10) Yellow crystals were obtained from a saturated acetone solution of complex **1** layered with hexane. Crystal data: $C_{27}H_6Au_2Cl_{20}OTl_2$, triclinic, $P-1$, $a = 11.4289(4)$ Å, $b = 12.2774(4)$ Å, $c = 14.3764(4)$ Å, $\alpha = 98.415(1)^\circ$, $\beta = 94.953(1)^\circ$, $\gamma = 91.618(1)^\circ$, $V = 1986.37(5)$ Å³, $Z = 2$, $\rho_{\text{calc}} = 3.106 \text{ Mg/m}^3$, $2\theta_{\text{max}} = 56^\circ$, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, ω and ϕ scans, $T = -100$ °C, 27624 measured reflections, 9100 independent reflections ($R_{\text{int}} = 0.0526$), with $I < 2\sigma(I)$, absorption correction (based on multiple scans) ($\mu = 16.825 \text{ mm}^{-1}$), 471 refined parameters with $R1 = 0.0566$ and $wR2 = 0.1491$, Goodness-of-fit on $F^2 = 1.111$. The structure was solved by direct methods with SHELXS-97 and refined with SHELXL-97 by full-matrix least-squares on F^2 with all the non-hydrogen atoms anisotropically defined. The hydrogen atoms were included in calculated positions, isotropically refined with common thermal parameters and allowed to ride on their present carbon atoms.
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