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Photophysical Studies and Excited-State Structure of a Blue Phosphorescent Gold–Thallium Complex

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The dinuclear complex $\{[\mathrm{Tl}(\eta^6\text{-toluene})][\mathrm{Au(C_6Cl_5)_2}]\}$ (**1**) displays very intense blue phosphorescence and a rigidochromic behavior in the solid state. The photophysical measurements in a glassy solution display an oligomerization process via metal–metal interactions. Density functional theory calculations show a distortion of the aurate–thallium T shape in the lowest triplet excited state, leading to a triplet metal-to-metal charge-transfer state.

For main-group metals in their low oxidation states, lone pairs of electrons play an important role in the geometry and chemical behavior and often become apparent by a distortion of regular coordination geometries or by a cation with ligands only coordinating one hemisphere.[1] Thus, thallium(I) complexes can show several structural arrangements of the ligands around the metal center, as is observed in the crystal structure of complexes between thallium and bis(pyrazolyl)borate or tris(pyrazolyl)borate, with planar trigonal, tetrahedral, or trigonal-bipyramidal distorted geometry around thallium(I), where the lone pair occupies the third, fourth, or fifth coordination position, respectively.[2,3]

In addition, gold(I)/thallium(I) heteronuclear systems represent an important class of materials with interesting photophysical properties and a large structural variety, such as loosely bound butterfly clusters,[4] 1D linear or zigzag polymeric chains,[5] or 2D and 3D arrays.[6]

In this work, we report the synthesis, luminescent properties, theoretical calculations, and crystal structure of the complex $\{[\mathrm{Tl}(\eta^6\text{-toluene})][\mathrm{Au(C_6Cl_5)_2}]\}$ (**1**), in which a discrete molecule with a short gold−thallium unsupported interaction is observed. The coordination hemisphere of thallium(I) is completed by an unusual η^6-arene contact to a toluene molecule. Thus, by reaction of a dichloromethane suspension of $\mathrm{TlPF_6}$ with $\mathrm{NBu_4[Au(C_6Cl_5)_2]}$, filtration of the yellow solid, and subsequent treatment of this with toluene, **1** was obtained as an ocher-colored solid (see the Supporting Information for details).

X-ray-quality crystals of **1** were obtained by slow diffusion of hexane in a saturated solution of the complex in toluene, which was allowed to univocally establish its crystal structure.[7] It consists of discrete dinuclear units of **1** in which the metal centers are joined via an unsupported Au···Tl contact and the toluene molecule interacts with each thallium(I) center in a η^6 mode (Figure 1and Table 1). The Au−Tl distance, of 2.9115(2) Å, is one of the shortest described to date,[8] being even shorter than the sum of the Au−Tl covalent radii (2.92[9a] or 3.08 Å[9b]), and is on the same order as those found in the discrete gold/thallium systems $[\mathrm{Tl\{Au_2(P_2\text{-}phen)_3\}](ClO_4)_3}$ ($\mathrm{P_2}$-phen = 2,9-bis(diphenylphosphino)-1,10-phenanthroline) (2.911−2.917 Å)[10] and $[\{\mathrm{AuTl(C_6Cl_5)_2(toluene)}\}_2$-

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(7) Crystal data of **1**: $\mathrm{C_{19}H_8AuCl_{10}Tl}$, triclinic, $P\bar{1}$, $a = 8.4051(2)$ Å, $b = 10.4775(2)$ Å, $c = 14.7541(3)$ Å, $\alpha = 76.352(1)°$, $\beta = 77.136(1)°$, $\gamma = 80.214(1)°$, $V = 1221.44(4)$ Å^3, $Z = 2$, $\mu = 13.689$ mm^{-1}, 19 226 reflections, $2\theta_{\max} = 56°$, 5790 unique ($R_{\mathrm{int}} = 0.0420$), R1 = 0.0299, $R_{\mathrm{w}} = 0.0690$ for 281 parameters, 88 restrictions, $S = 1.027$, max $\Delta\rho = 2.401$ e Å^{-3}. Crystal data of **1** were measured at −50 °C using a Nonius Kappa CCD diffractometer, Mo Kα radiation, and ω and ϕ scans. The structure was solved by direct methods and refined anisotropically on F^2 (Sheldick, G. M. *SHELXL-97*, University of Göttingen: Göttingen, Germany, 1997). Absorption correction: multiscan.

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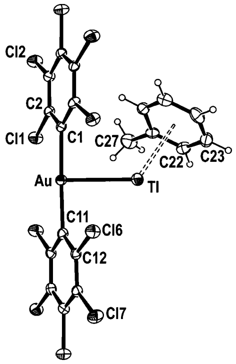

Figure 1. Crystal structure of **1**. Selected bond lengths [Å]: Au−Tl 2.9115(3), Au−C1 2.051(5), Au−C11 2.051(5), Tl−Ct 3.068.

Table 1. Experimental and Theoretical Structural Parameters (Distance in Angstroms and Angles in Degrees)

state	Au···Tl	Au−C	Tl···C	C−Au−C
experiment	2.91	2.05	3.28−3.46	176.9
singlet (S_0)	2.86	2.09	3.57	179.3
triplet (T_1)	3.30	2.17	3.63	121.7

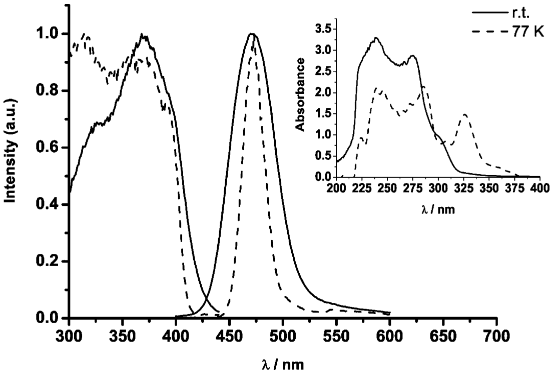

Figure 2. Excitation and emission spectra of **1** at room temperature (solid line) and 77 K (dashed line) in the solid state. Inset: Absorption spectra of **1** in EtOH/MeOH (4:1) at room temperature (solid line) and 77 K (dashed line).

(dioxane)] [2.8935(3) Å].[11] Each Tl atom interacts with a toluene molecule in an unusual η^6-like π-arene mode with Tl−C distances in the range of 3.281(5)−3.458(5) Å (Tl−Ct = 3.068 Å), similar to those observed in the few examples of η^6-like π-arene thallium complexes described to date.[11,12] The gold(I) center displays its typical linear coordination, and both gold(I) and thallium(I) keep additional M···Cl contacts in the ranges of 3.281(1)−3.347(1) and 3.332(1)−3.530(1) Å. Finally, the shortest Au···Au distance, 3.4625(2) Å, rules out the presence of intermolecular metallophilic contacts.

As expected by our preliminary work in similar systems, complex **1** shows a very intense luminescence in the solid state, although it displays an unconventional behavior if compared with other gold/thallium complexes.[4−6] It is strongly luminescent at room temperature (Figure 2) and at 77 K in the solid state, displaying a broad and unstructured emission in the blue region at 470 nm (maximum excitation at 370 nm) and a narrower band at similar emission and excitation energies at 77 K, respectively, showing an interesting *rigidochromic effect*.[13,14] Although the reason of this phenomenon in the solid state is not fully understood, some authors suggest[14] that the emission energy maximum depends on the environmental rigidity. In this sense, usually at lower temperatures, the metal−metal distances are expected to decrease, producing a red shift of the emission bands. The very short experimental Au−Tl distance found in this case could be the reason why this observation is prevented in this complex.

The excitation spectrum of the complex shows a complicated profile with an emission independent of the excitation wavelength. The less energetic zone of the excitation spectrum is significantly red-shifted from the major absorption bands seen in solution as well as in glass at 77 K, indicating that those transitions are forbidden and, therefore, in accordance with phosphorescent processes. In this regard, the lifetime in the solid state at room temperature agrees with this proposal because it fits a biexponential decay with values of 14.5 ± 0.5 and 2.5 ± 0.2 μs ($R^2 = 0.998$).

What is usual in extended systems of these two metals is that they lose the optical properties by rupture of the Au···Tl interactions when dissolved in solvents with donor characteristics,[5,6] while in nondonor solvents, they are insoluble. Nevertheless, in this case, complex **1** is luminescent in toluene, showing a band at 490 nm with a small shoulder in the less energetic zone. The value close to that found in the solid state (470 nm) seems to suggest similar emissive states, although slightly influenced by the dipole moment of the solvent. The evaporation of the solvent regenerates **1** in a quantitative yield.

A different behavior is observed in alcohols at low temperature because the measurement carried out in a glassy EtOH/MeOH (4:1) solution at 77 K is concentration-dependent. Thus, when the measurement is carried out in a concentration of 4×10^{-5} M, an emission at 475 nm appears (maximum excitation of 325 nm), but increments of the concentration to 4×10^{-4} M lead to an additional and independent emission at 515 nm (maximum excitation of 360 nm), increasing the intensity of the lower-energy band as the concentration increases. This result is likely due to the presence of oligomers of different lengths or, alternatively, to complex **1** (470 nm) and to an oligomer responsible for the low-energy band, respectively. As has been previously reported, as the number of metal−metal interactions increases, the emission wavelengths are shifted to lower energies. The spectrum of the precursor complex $[AuTl(C_6Cl_5)_2]_n$, under similar conditions, displays only one emission at 515 nm. In this case, the evaporation of the solvents does not lead to complex **1** and instead the gold/thallium precursor appears.

Also, the absorption spectra in degassed EtOH/MeOH (4:1) (inset in Figure 2), at room temperature, of complex **1** and the precursor derivative display identical profiles with absorptions at 240 nm ($\epsilon = 6.3 \times 10^3$ mol^{-1} dm^3 cm^{-1}),

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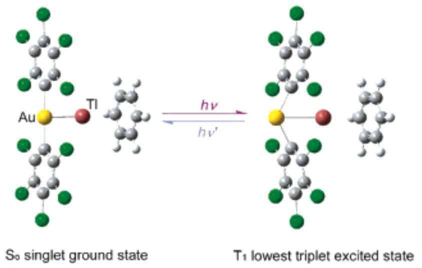

Figure 3. DFT-optimized structures for the singlet ground state and the lowest triplet excited state.

278 nm ($\epsilon = 5.7 \times 10^3$ mol^{-1} dm^3 cm^{-1}), and 301 nm ($\epsilon = 3.7 \times 10^3$ mol^{-1} dm^3 cm^{-1}), peaks that appear at wavelengths similar to those in the precursor $NBu_4[Au(C_6Cl_5)_2]$ complex in the same solvents, and, therefore, we assign them tentatively to $\pi\pi^*$ transitions located in the pentachlorophenyl rings. By contrast, the absorption spectrum of the glassy solution at 77 K shows, in addition, the presence of an additional band at 325 nm, of small intensity, whose position matches one of the excitation maxima found under the same experimental conditions. This fact could indicate that this absorption is responsible for one of the observed emission bands (475 nm) and is related to the formation of Au−Tl interactions, because the precursor gold and thallium complexes do not show this absorption, although it might be caused by aggregation giving rise to oligomers. Similarly, complex $[\{AuTl(C_6Cl_5)_2(toluene)\}_2(dioxane)]$ displays an analogous optical behavior, indicating a similar origin.[11] The photophysical properties of **1** have been measured several times in samples prepared separately, giving rise in all cases to similar results. Therefore, this fact seems to rule out the possibility of a luminescent impurity in the bulk material.

We carried out density functional theory (DFT)/B3LYP calculations to study the geometries for the ground state and the lowest triplet excited state for **1** in order to gain insight about the mechanism responsible for the phosphorescent behavior observed experimentally.

First, we have fully optimized the model system $\{[Tl(\eta^6\text{-}benzene)][Au(C_6Cl_5)_2]\}$ (**1A**; C_{2v} symmetry) in the ground and first triplet excited states at the DFT level of theory. The optimized ground state for model **1A** displays a T-shaped disposition for the aurate/thallium moiety in which a Au···Tl interaction of 2.86 Å (exptl 2.91 Å) is achieved (see the Supporting Information). On the other hand, full optimization of the first triplet excited state displays a distortion of the aurate/thallium T shape through an increase of the Au···Tl distance (3.30 Å) together with a bend outward of the C−Au−C angle from linear 180° to 121.7° (see Figure 3). This result is similar to the one proposed by Omary et al. for $[Au(PR_3)_2X]$ complexes[15] in which a distortion *beyond a T shape* of the tricoordinated gold(I) center is reached in the emissive lowest triplet excited state.

The analysis of the frontier orbitals for both the ground and triplet excited states for **1** has been carried out. In the ground state (S_0), the highest occupied molecular orbital (HOMO) is localized on the $[Au(C_6Cl_5)_2]^-$ fragment, while the lowest unoccupied molecular orbital is mainly placed at the Tl^+ ion. On the other hand, upon excitation of one electron to the lowest triplet excited state (T_1), the shape of the SOMO−1 orbital (SOMO = singly occupied molecular orbital) remains at the aurate, while the SOMO orbital is located at the metal centers (see Figure 4). These electronic structures together with the lowest triplet excited-state distortion can be interpreted in terms of a charge transfer from the aurate (doubly occupied HOMO in the ground state) to the metal centers, as can be observed in the shape of the 95a orbital for the T_1 state. In this way, upon charge transfer, the system loses the strong ionic interaction between the metals and, therefore, the intermetallic Au···Tl distance increases.

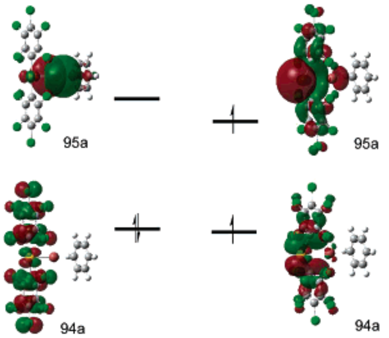

Figure 4. Molecular orbital diagrams for the ground state S_0 (left) and the lowest triplet excited state T_1 (right).

The theoretical results shown here on the charge-transfer character of the transition responsible for the luminescent behavior are in agreement with the reported experimental data of complex **1**. In contrast to already reported polymeric chains, gold/thallium systems of alternating metals in which the luminescence is attributed to a fluorescent process with lifetimes in the nanoseconds range, complex **1** represents an example of a discrete Au−Tl system in which the luminescence arises from a T_1 excited state, giving rise to a phosphorescent process. In this regard, the optimization of the lowest triplet excited state shows how the $[Au(C_6Cl_5)_2]^-$ moiety bends outward. This trend would not be possible in the case of a polymeric system because the aurate unit is always placed between two acidic Tl^+ ions, which may prevent the bend of the C−Au−C angle and a Au−Tl distance enlargement.

In conclusion, with regard to the presented data and taking into account the theoretical calculations, we assign the emission in the solid state as arising from a triplet metal-to-metal charge-transfer state, from the electron-rich bis(perchlorophenyl)gold(I) anion to the metals gold(I) and thallium(I).

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Supporting Information Available: X-ray crystallographic data in CIF format for **1**; experimental procedure, characterization data, photophysical measurements, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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