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Electronic structure and luminescence of $[AuS_2PPh(OCH_2CH{=}CH_2)]_2$ complex

Jesús Muñiz *, Luis Enrique Sansores, Ana Martínez, Roberto Salcedo

Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apartado Postal 70-360, México DF 04510, Mexico

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Abstract

The complex $[AuS_2PPh(OCH_2CH{=}CH_2)]_2$ (**1**) presents an Au(I)–Au(I) intramolecular and intermolecular bonding with luminescence properties. To understand the nature of these features, fully optimized geometries were obtained by three computational methods, DFT/B3LYP, MPW1B95 and MP2. An Au(I)–Au(I) intramolecular bond was found in the ground state, at the three levels of theory, exhibiting an aurophilic interaction between the two gold atoms. Two molecules of the complex were optimized using DFT/B3LYP, in order to analyze the intermolecular interaction between them. The resulting intermolecular bonding distance between the two adjacent gold atoms on each molecule is 3.16 Å, indicating a strong aurophilic attraction. Time dependent calculations indicate that the first excited state with nonzero oscillator strength is a singlet, with an excitation energy equal to 3.16 eV. This should correspond to the absorption band seen experimentally at 3.10 eV. The lowest energy emission of (**1**) was obtained at 2.73 eV, which corresponds to the emission peak resulting from phosphorescence and located at 2.53 eV. This transition comes from an excited electron on the p orbitals of the ligands that is transferred to the d orbitals of the gold atoms on the HOMO. This interaction may be attributed to Ligand to Ligand–Metal Charge Transfer (LL–MCT).

Keywords: Aurophilic interactions; TD DFT; Triplet; LL–MCT

1. Introduction

Gold(I) compounds have a wide range of applications, such as the incorporation of these complexes in the design of electronic and sensor devices [1–3], photographic emulsions [4–6], biosensors [7], photocatalysts [8], gold-based drugs for anti-arthritic treatment [9–12] and chemotherapy. As an example, the oral drug, Auranofin, which is used in the treatment of rheumatoid arthritis, has a neutral Au(I) thiolate complex, where the bond between Au(I) and one cysteine of the protein is emphasized to exert the therapeutic action [10–12]. A deeper understanding of the features of these compounds, which are related to their electronic structure and excited state properties, is of great importance, since the chemistry of most Au(I) compounds is ruled by a phenomenon termed *aurophilicity*, which has its origins in relativistic and correlation effects [13–17]. Aurophilicity is characterized by a bond length contraction between two or more gold atoms inside the molecule, showing intramolecular interaction [18,19], and is also observed between gold atoms on adjacent molecules, presenting intermolecular interaction. The aurophilic interaction has also been studied, by Hoffmann et al. [20–24], Evans and Mingos [25], Burdett et al. [26] and Cui and Kertesz [27], in theoretical works at the one-electron level of extended Hückel molecular orbital theory. Those authors studied several closed-shell complexes where the Au(I)–Au(I), Cu(I)–Cu(I), In(I)–In(I), Tl(I)–Tl(I) and Pt(0)–Pt(0) interactions are present.

It was found that an orbital mixing of the *n*d and $(n+1)$s and p orbitals is responsible for the closed-shell attraction, where the HOMO and LUMO interactions play

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* Corresponding author. Tel.: +52 55 55 50 1935; fax: +52 55 56 16 07 54.
E-mail address: jesus@iim.unam.mx (J. Muñiz).

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an important role. In particular, the Au–Au interaction comes from the mixing of the filled 5d orbital and the empty 6s and 6p shells.

Aurophilic compounds show a weak attractive Au(I)···Au(I) interaction, with a dissociation energy of 5–15 kcal/mol [28–30], comparable with the dissociation energy of hydrogen bonds. When the aurophilic interaction energy dominates the energies associated with crystal packing effects, weak interactions will be present in the crystalline solid [30]. A major feature of this these types of complexes is their luminescence properties, which in most instances appears to be governed by aurophilic interactions, although there are some examples where the opposite seems to be the case. The complex under study is $[AuS_2PPh(OCH_2CH{=}CH_2)]_2$ (**1**), a neutral eight-membered, metallocyclic, dinuclear gold(I) compound [30], which can be seen in Fig. 1.

It has an elongated chair conformation with a weak transannular gold–gold (~3.1 Å) interaction.

The synthesis of complex **1** was reported by van Zyl et al. [30]. X-ray studies reveal the presence of intra and intermolecular Au···Au interactions in the solid state. Spectroscopic measurements reveal that the complex is luminescent at room temperature and at 77 K. An absorption band is located at 400 nm (3.10 eV). At room temperature, an emission band is located at 443 nm (2.80 eV), while at 77 K, two peaks in the emission band were reported: at 445 nm (2.79 eV), and at 491 nm (2.53 eV). The high energy band appears to result from fluorescence, and the lower energy band from phosphorescence.

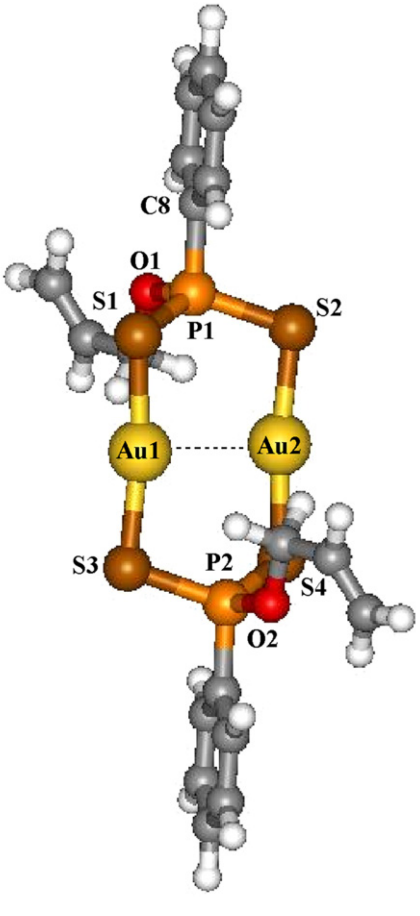

Fig. 1. Complex **1** after geometry optimization with the B3LYP/B1 computational method.

Experimental results suggest that the emission spectra is produced by an excitation originating from an orbital on the sulfur atom of the ligand, and not from a π orbital of the phenyl group. This is assumed from the comparison with analogue dinuclear Au(I) systems [30,31] that also contain phenyl groups. A significant change in the energies of the emission bands of these complexes is observed. An excitation emanating from the phenyl groups would be expected if the emission energy of both compounds were similar. Due to the large difference in the emission energies of the two compounds, the authors attributed the emission to a charge transfer process from the Ligand to the Metal (LMCT process), similar to other dinuclear Au(I) compounds bonded to sulfur, which present a transition associated with a sulfur to the metal-based orbital in the excited state. The spectroscopic properties of compound **1** are related to the presence of aurophilic interactions, i.e., the aurophilic attraction produces, as a result, the luminescence observed in this complex.

Theoretical studies directed toward understanding the aurophilic interaction and luminescence properties of compound **1** are not available. The aim of this work is to arrive at an understanding of the bonding properties of complex **1**, and the nature of the electronic transitions involved in the absorption and emission bands observed in the experiment, by using electronic structure calculations.

2. Computational methods

The optimized geometries were obtained with the B3LYP functional [32], which combines the exact Hartree-Fock exchange with the Lee, Yang and Parr correlation functional that includes the most important correlation effects. Geometry optimizations of complex **1** were also performed, using two different approaches: The Zhao–Truhlar hybrid meta functional MPW1B95 [33], which was developed in order to produce a better performance where weak interactions are involved, and the MP2 (Møller–Plesset second order perturbation) method [34], which accounts for explicit dispersion effects. Basis set superposition errors were calculated using the counterpoise method [35]. The pseudopotential LANL2DZ [36], with 19 valence electrons, was used for the Au atoms in order to include relativistic effects. The Stuttgart small-core pseudorelativistic effective core potential [37] with 19 valence electrons was also used for Au, with the optimized contracted Gaussian basis set of Schäfer et al. [38]: The valence triple-ζ plus one polarization type, TZVP. This basis set was augmented with two additional f-type polarization functions ($\alpha_f = 0.2$, 1.19), which were calculated by Pyykkö et al. [39]. The former function is a diffuse f orbital