

Theoretical study of the electronic structure and luminescence of trinuclear gold complex

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Abstract

The luminescence of the trimeric organometallic complex $[\text{Au}_3(\text{CH}_3\text{N}_y\text{COCH}_3)_3]$ in solution has been reported recently. To explain this phenomenon, we have carried out theoretical calculations of the complex in gas phase and in chloroform solution at B3LYP/6-31++G level. The calculated structure and the vibrational frequencies are in good agreement with the experimental results. Calculation of the triplet as the excited state gives an emission transition equal to 2.34 eV in gas phase and 2.36 eV in solution. With these results, a possible explanation of the luminescence of this compound is given. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The trimeric organometallic complex $[\text{Au}_3(\text{CH}_3\text{N}_y\text{COCH}_3)_3]$ (compound **1**) was first synthesized and characterized in 1974 [1,2]. Blach et al. have carried several studies on this compound [3–5] and found a very interesting feature, the solvoluminescence [3,6], i.e. the luminescence induced by contact with a solvent (chloroform) after excitation with the UV light. To shed some insight on the origin of the emission they [3,6] carried out spectroscopic measurements. They reported three emission spectra: (1) from the solution of **1** in chloroform; (2) from a polycrystalline sample of **1**; and (3) of the light

emitted from a polycrystalline sample of **1** after the UV irradiation and contact with a drop of chloroform. In summary, the emission spectrum of **1** in chloroform shows a peak centered at 422 nm (2.94 eV). The excitation wavelength for the emission spectrum is 250 nm (4.96 eV). The emission spectrum of the polycrystalline sample has two peaks at 446 nm (2.78 eV) and 552 nm (2.25 eV). The excitation is a broad peak centered at 380 nm (3.26 eV). Comparison of these results suggests that the properties of this complex in the crystalline solid are significantly different from those of the solution. The yellow light emitted from a polycrystalline sample of **1** after UV irradiation and in contact with a drop of chloroform is also centered at 552 nm (2.25 eV). Characterization of the structure was carried out by X-ray diffraction on a single crystal.

The solvoluminescence exhibited by **1** is a remarkable new phenomenon that justifies further examination, especially because the source of the effect is not

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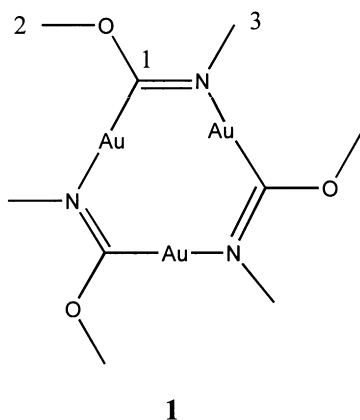


Fig. 1. Compound under study after geometry optimization.

yet clearly established and there are no theoretical studies, although many applications of this emission are possible. For this reason, the understanding of the origin of the luminescence is very important. To give some insight on the properties of this compound, in this paper we report a theoretical study of the electronic structure of compound **1**.

2. Methodology

All calculations were performed using GAUSSIAN 94 [7] at the B3LYP level. The basis used for carbon, nitrogen, oxygen and hydrogen atoms were 6-31G with diffuse functions (6-31G++). For gold, the basis used was LANL2DZ [8–10] with pseudopotential considering explicitly 19 valence electrons. Optimized geometries were verified by frequency

calculations and also by geometry optimization without symmetry constrains. Frequencies calculations were carried out using a 6-31G* and LANL2DZ. To model the compound in solution we have used the isodensity Tomasi's polarized continuous model [11,12].

3. Results and discussion

The optimized structure of compound **1** is shown in Fig. 1. The molecule is completely planar with C_{3h} symmetry. Only the hydrogen atoms attached to the carbons are out of the plane. In Table 1, distances and angles are listed together with the experimental results of X-ray diffraction. As it can be noted, the experimental and theoretical results are in good agreement (an average error in the bond distance of 0.300 Å), the larger difference, 0.066 Å is in the Au–N distance. The bond length between C1 and the neighboring nitrogen is reasonable for a double bond. With respect to the angles there is a slight dispersion in comparison with the experimental values although the agreement is good. The angles centered at C1 are distorted with respect to the sp^2 hybridization, while those centered at the N are very close to the correct value. This means that the presence of the Au atom is distorting the hybridization of the near neighbor carbon atom.

In Table 2 we compare the frequencies of our infrared spectrum with those obtained experimentally. In our calculations we have used a value of 0.94 for the scale factor. There is a good agreement between theory and experiment (the average error is 42 cm^{-1} and maximum deviation of 60 cm^{-1}). The small

Table 1
Distances and angles in a molecule of compound **1**

Distances	Theory	Experimental [3]	Angles	Theory	Experimental [3]
Au–C1	2.026	2.00	N–Au–C1	178.3	180.0
Au–N	2.098	2.03	Au–C1–N	122.3	119.4
C1–N	1.313	1.29	C1–N–Au	119.5	120.6
N–C3	1.485	1.48	Au–C1–O	124.2	121.4
C1–O	1.386	1.36	C1–O–C2	119.4	115.3
O–C2	1.463	1.43	C1–N–C3	120.2	118.6
			Au–Au–Au	60.0	60.0
			N–Au–C1–N	0.0	0.0
			Au–C1–N–Au	0.0	0.0
			Au–C1–N–C3	–180.0	–180.0
			Au–C1–O–C2	0.0	0.0

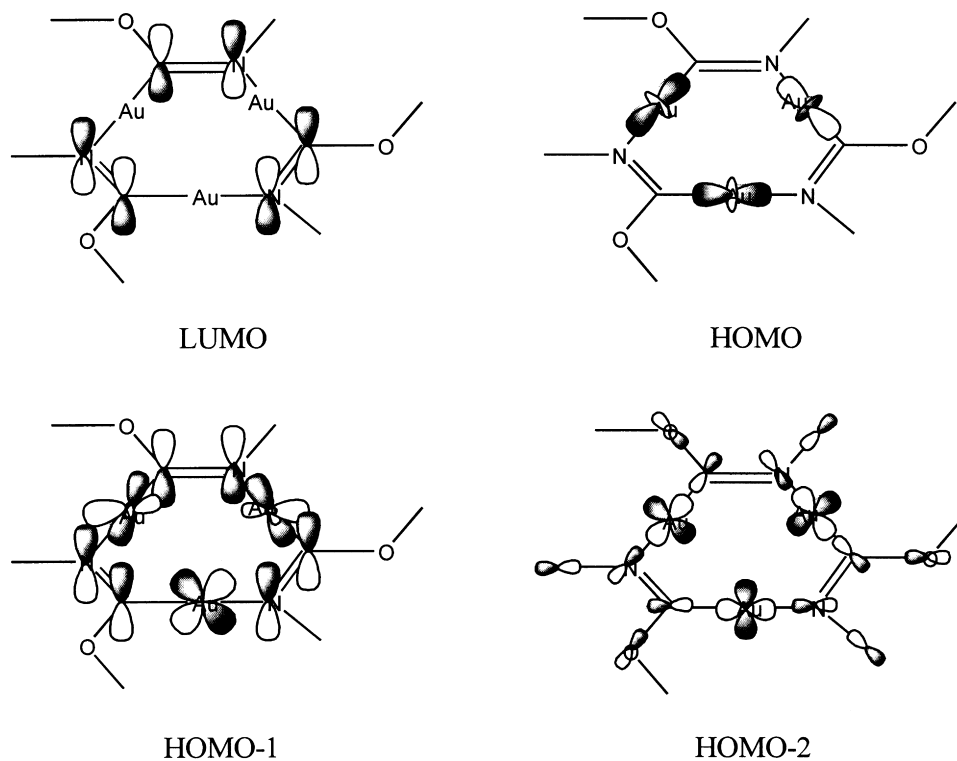


Fig. 2. Spatial distributions of the molecular orbitals near the occupation edge of compound **1** in the ground state configuration.

differences may be due to the fact that experimental determination was carried out in polycrystalline samples, while calculated geometries are in gas phase. This agreement, and the fact that we do not have imaginary frequencies indicate that the theoretical model corresponds to that observed experimentally.

Fig. 2 shows the spatial distribution of some molecular orbitals near the occupation edge. The LUMO belongs to the e'' irreducible representation. It is

mainly located at the C and N atoms and is the anti-bonding π orbital. The HOMO belongs to the e' irreducible representation and has its main contributions from the d_{z^2} atomic orbitals of the gold atoms. The HOMO-1 belongs also to the e'' irreducible representation. It has contributions from all the atoms of the rings. The gold atoms contribution is d_{xz} and there is a π bonding interaction between the carbon and the nitrogen. The bonding between the carbon and nitrogen atoms with the gold atoms is due to the interaction

Table 2
Infrared data comparison (cm^{-1})

	Theory	Experimental
$\nu(\text{C}-\text{OMe})$	1173	1125 [1]
$\nu(\text{C}\gamma\text{N})$	1499	1565 [1], 1569 [2]
$\nu(\text{C}-\text{H})$	2850	2826 [2]
$\nu(\text{C}-\text{H})$	2903	2871 [2]
$\nu(\text{C}-\text{H})$	2923	2925 [2]
$\nu(\text{C}-\text{H})$	2950	2982 [2]

Table 3
Charges for compound **1** in ground state

Atom	Charge
Au	-0.547
N	-0.128
C1	0.497
Me2	0.203
Me3	0.253
O	-0.279

Table 4

Electronic parameters: E_T is the total energy; ΔE the energy difference between the HOMO and LUMO (for the triplets it is the energy difference between the α -HOMO and β -LUMO); and ΔE_T is the difference in total energy with respect to the corresponding ground state

	Gas phase	Solution	Triplet	Trip. sol.
E_T (eV)	-31 293.31	-31 292.88	-31 288.99	-31 288.82
ΔE (eV)	5.635	5.40	2.34	2.36
ΔE_T (eV)	0.0	0.0	4.32	4.06
Dipole (D)	0.0	2.01	2.10	5.17

between the $d_{x^2-y^2}$ of the gold and the p_x of the C and N atoms as seen in the HOMO-2 that has an a' irreducible representation.

In Table 3, we present the results of the Mulliken charge analysis. It is important to note that the gold is negatively charged almost with the same charge that the carbon on the ring is positively charged. The nitrogen and oxygen atoms are negatively charged and the two methyl groups are positively charged. This means that the gold atoms are draining charge from the carbons and thus some hybridization of the carbons is lost.

To understand the emission spectra of the compound, two types of calculations were done: B3LYP calculations of the electronic structure of the triplet state and a CIS (singlets and triplets), both with the basis described above and without geometry optimization. At the B3LYP level, the difference in total energies between the ground state and the triplet is 4.32 eV (see Table 4). From the CIS calculation, the first excited state is a triplet with 4.446 eV excitation energy and oscillator strength of 0.0. The first non-zero oscillator strength excited state is a singlet with 6.28 eV excitation energy (see Table 5).

As the emission spectrum was measured in a chloroform solution, calculations of the ground state

Table 5

Excitation energies, wavelength (λ) and oscillator strength (f) of the excited states given by the CIS calculation

	Energy (eV)	λ (nm)	f
Triplet	4.446	278.9	0.00
Triplet ^a	4.504	275.3	0.00
Triplet	5.019	247.0	0.00
Triplet	5.082	244.0	0.00
Singlet ^a	6.162	201.2	0.00
Singlet	6.283	197.3	0.213
Singlet ^a	6.638	186.8	0.078

^a Doubly degenerate.

and the triplet state of compound **1** in chloroform solution were done. The results are summarized in Table 4. It should be noticed that in solution the ground state of the compound presents a dipole moment, this is a necessary condition for the compound to be soluble. The total energy of the molecule in solution is higher than that of the gas phase, as the polarization of the molecule breaks the orbital symmetry. The triplet state in solution has almost the same total energy of the triplet state in gas phase, so the singlet–triplet splitting value is 4.06 eV, slightly smaller than for the gas phase.

The orbital energies of the triplet state show that there is a two-step transition from the triplet state to the ground state (see Fig. 3) the α -HOMO of the triplet is single occupied and has a higher energy than the β -LUMO that is unoccupied. In the solid, these two energy levels would correspond to an excitonic state and the emission spectra could be generated by the transition of one electron from the α -HOMO to the β -LUMO of the triplet state. The energy gap between these two orbitals is equal to 2.34 eV in the gas phase and 2.36 eV in the chloroform solution.

The resulting picture is that, in solution, the absorption experimentally seen at 4.96 eV (259 nm) [6] corresponds to the excitation of the triplet state calculated as 4.06 eV and the emission found at 2.94 eV (422 nm) [6] to the transition from the triplet to the ground state, that is, the α -HOMO to the β -LUMO calculated as 2.36 eV. As the oscillator strength for this transition is very small this should be a weak and long lived emission in agreement with the experimental observation [1].

4. Conclusions

The results of the geometry optimization of compound **1** are in good agreement with the X-ray

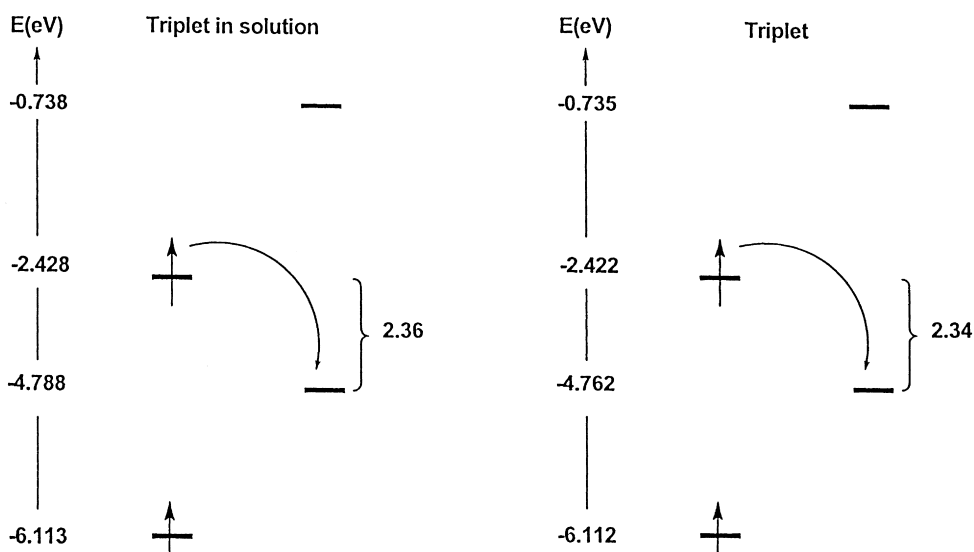


Fig. 3. Molecular orbital energy scheme for the triplet state in solution and in gas phase.

experimental results. Calculations of the ground state and the triplet state of compound **1** in chloroform solution were done. The absorption spectrum is describe by transitions from the ground state to the triplet state while the emission spectrum is describe by the transition from the triplet state to the ground state with reasonable agreement with the experimental values.

The orbital energies of the triplet and singlet states show that there is a two-step transition from the triplet state to the ground state. It can be noted that the α -HOMO of the triplet presents higher energy than the β -LUMO. The emission spectra can be generated by the transition of one electron from the α -HOMO to the β -LUMO of the triplet state. With these results, it is possible to consider that in the solid the triplet state corresponds to an excitonic state and that the solvoluminescence emission is due to the recombination of the exciton triggered by the solvent. Further studies in the solid state phase necessary for an understanding of the solvoluminescence present in compound **1** are being carried out.

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