Electronic structure of triangular trigold(I) complexes. A theoretical study

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Abstract

Triangular trigold(I) complexes have been synthesized and characterized by several authors. These molecules have linear two-coordinated gold(I) centers connected by bridging ligands to form nine-membered rings. Although this type of molecules have been known for more than 20 years, some remarkable properties have attracted new interest. $Au_3(CH_3N=COCH_3)_3$ shows solvoluminescence, supramolecular association and some $(\mu\text{-pz-}N,N)_3Au_3$ form mesophases with hexagonal columnar structures with weak dimer formation. In this work we study the electronic structure of these molecules. We also include $[Au(\mu\text{-}N^3,C^2\text{-bzim})]_3$ and $[2\text{-pyridyl-Au}]_3$. Calculations were done at B3LYP level with $6\text{-}31++G$ basis for all atoms except Au where LAN2LDZ was used. Geometry optimization shows that all molecules are flat and highly symmetric. For molecules **1** and **4** the LUMO is mainly located on the rings and the HOMO main contributions are from the Au atoms. In molecules **2** and **3** the LUMO main contributions are from the gold's. An electronic delocalization similar to aromaticity is found in the nine-member ring of all compounds. This effect is studied with the NICS index.
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1. Introduction

The chemistry of pyrazole and pyrazolate compounds is quite extensive and has been studied for more than 20 years. In particular, trinuclear gold compounds have attracted renewed attention due to recent reports of novel properties [1–18] such as: solvoluminescence, supra molecular association and columnar mesophases. Four good examples are those shown in Fig. 1, that is the matter of this report.

The trimeric organometallic complex $[Au_3(CH_3\text{-}N=COCH_3)_3]$ (Compound **1**) was first synthesized and characterized in 1974 [1,2]. Balch et al. have carried several studies and found the interesting effect of solvoluminescence [3–7]. Crystals of **1** were irradiated with near-UV light; after irradiation, a long-lived photoluminescence was found. Addition of a solvent to the irradiated crystals produces a bright burst of yellow light. Their X-Ray studies show that in solid state this compound has a columnar structure. This complex undergoes oxidative addition of halogens to form mixed valence complexes of the type $Au^I_2Au^{III}I_2L_3$, $Au^IAu^{III}_2\text{-}I_4L_3$ and $Au^{III}_3I_6L_3$ [4,5]. The electronic structure and a

possible explanation for the luminescence of compound **1** has been reported previously by our group [8]. To explain the luminescence, theoretical calculations of the complex in gas phase and in solution were done (the simulated solvent was chloroform). We concluded that the yellow light emission corresponds to a triplet state that in the solid is an excitonic state. The solvoluminescence emission is due to the recombination of the exciton triggered by the solvent.

Pyrazolate complexes of the type **2** have attracted attention since they form columnar mesophases at room temperature [9,10]. For this type of compounds, Bovio et al. [11] reported the synthesis and X-Ray characterization of tris[µ-3,5-bis(trifluoromethyl)pyrazolato-N,N']trigold(I) and later Murray et al. [12] reported similar characterization for tris[µ-3,5-diphenylpyrazolato-N,N']trigold(I). The first found a non-planar ring and no crystallographic symmetry, while the later, found that the molecule belongs to the D_{3h} point group and has a rigorously planar nine member ring. Complexes with longer side branches, which show the mesophases, have also been characterized [9,10]. In other words the side chains are very important for the structure and properties of these compounds. With respect to the chemical reactivity, complex **2** only form the $Au^I_2Au^{III}Cl_2L_3$ compound [13]. In 2005, Omary et al. [14] reported the X-Ray structure of a similar fluorinated derivative including a discussion concerning the luminescence behavior. They concluded that luminescence

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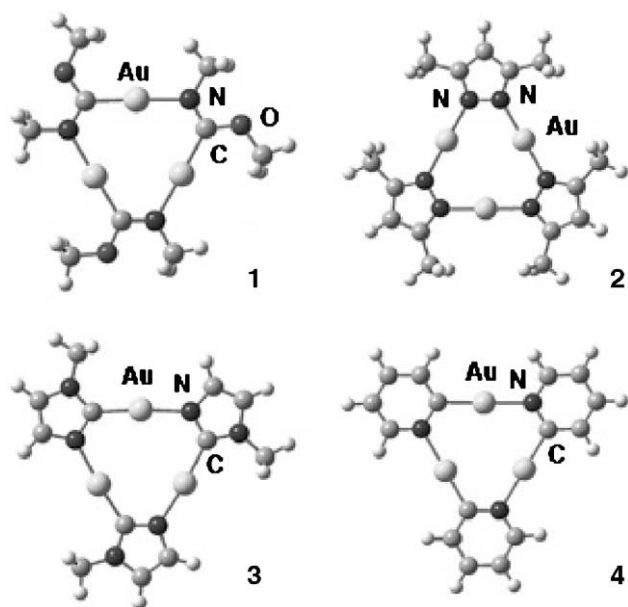*E-mail address:* sansores@servidor.unam.mx (L.E. Sansores).

Fig. 1. Compounds under study.

variations of the crystals are related to relaxations between the different excimers that enhance the metal–metal bonding.

Complex **3** was first synthesized by Bonati et al. [15]. The characterization was made by elemental analysis and ^{1}H and ^{13}C NMR. In 1991, the same authors [16] reported the oxidative addition reactions with this complex. They found that reaction with chlorocarbonate or ethyl iodide breaks the Au–N bond, and mononuclear compounds were obtained. Nevertheless, upon reaction with I_2 they reported the formation of $Au^I_2Au^{III}I_2L_3$ and $Au^IAu^{III}_2I_4L_3$. The only X-Ray structure reported is for tris-μ-(1-benzyllimidazolato-N^3,C^2)-diiodogold (III)gold(I) [17].

There is only one report about complex **4** by Vaughan. In 1970 [18] he described the synthesis of 2-pyridylgold(I) and concluded that the simplest structure consistent with the coordination requirements is that depicted in Fig. 1. There are no X-Ray results for this complex.

From the experimental results reported previously, the structures and chemical properties of these compounds are very attractive. Nevertheless, there are few theoretical results that can explain this interesting chemistry. For this reason, the purpose of this work is to analyze the electronic structure of complexes **2–4**. We include some previously reported and new

results of complex **1** for comparison. In order to understand the chemical properties, optimized geometries, natural bond atomic charges (NBO), molecular orbitals and nucleus independent chemical shifts (NICS) for each compound are reported.

2. Computational method

All density functional (DFT) calculations were carried out at B3LYP/6-31G(d,p) level [19] which combines the exact Hartree–Fock exchange with Becke's and uses the Lee-Yang-Parr correlation function in order to include the most important correlation effects. The version used was that included in the Gaussian03 code [20]. For gold atoms, the basis is LAN2LDZ that includes relativistic effects [21].

In general, DFT methods do not describe adequately dispersion-induced bonding. Nevertheless, these compounds can be reasonably well described by DFT due to the important back bonding characteristic. For compound **1** calculations at MP2 level were done and the geometry predicted is in very good agreement with that of the DFT. Similar results have been reported by Omary [14].

There is no universally accepted method of calculating atomic charges, and no experimental technique is available to measure them directly. In this paper, atomic charges were evaluated through the natural bond orbital (NBO) method [22].

As has been shown by several authors [23] the concept of aromaticity is not limited to fully conjugated organic rings. To characterize the aromaticity, Schleyer and coworkers [24] have used the NICS in cooper rings. In this work, the NICS were calculated following Schleyer et al. [25].

3. Results and discussion

All compounds under consideration are singlets and neutral. Geometry optimization, Fig. 1, shows that the four molecules are symmetric and flat. Symmetry for compounds **1**, **3** and **4** is C_{3h} while compound **2** has D_{3h}. Selected bond distances and angles are reported in Table 1. Comparison with experimental data [3,12,17] shows good agreement. The Au–C and Au–N bond lengths are similar for all compounds. The Au–Au distance varies between 3.429 for compound **1** and 3.472 Å for compound **2** indicating that there is an interaction among gold(I) atoms in all the compounds.

Table 1
Distances (Å) and angles (°)

Compound	1		2		3		4
	Theory	Exp.[3]	Theory	Exp.[12]	Theory	Exp.[16]	Theory
Au–C(N′)	2.026	2.00	2.039	1.978	2.012	2.02	2.022
Au–N	2.098	2.03	2.039	1.978	2.084	2.06	2.122
N–C(N′)	1.313	1.29	1.393	1.38	1.366	1.40	1.379
Au–Au	3.429	3.308	3.472	3.368	3.572	3.464	3.433
N–Au–C(N′)	178.3	180	178.7	179.6	174.8	175.6	179.4
Au–C(N′)–N	122.3	119.4	120.6	120.2	123.9	119.4	119.7
C(N′)–N–Au	119.5	120.6	120.6	120.2	121.3	119.9	119.7
Au–Au–Au	60.0	60.0	60.0	60.0	60.0	–	60.0

Table 2
Calculated distances (Å) and angles (°) of the rings

Compound	2	3	4
N1–C(N)2	1.393	1.366	1.379
C(N)2–C(N)3	1.361	1.378	1.415
C(N)3–C4	1.404	1.397	1.395
C4–C5	1.404	1.371	1.403
C5–N1(C6)	1.361	1.395	1.389
C6–N1			1.363
N1–C(N)2–C(N)3	108.4	106.6	117.5
C(N)2–C(N)3–C4	108.3	109.8	121.6
C(N)3–C4–C5	106.6	106.3	119.1
C4–C5–C1	108.3	108.2	118.3
C5–N1–C(N)2	108.4	109.1	
C5–C6–N1			122.3
C6–N1–C2			121.2

Bond distances and angles on the side rings are included in Table 2. The values indicate that the compounds are completely flat and fairly symmetric. The bond lengths are similar and typical of double bonds. This indicates electronic delocalization in the inner and side rings that can be correlated with the presence of aromaticity. This peculiar aromaticity in rings containing Au atoms has been observed in similar cases [26].

Figs. 2–4 show the HOMO-1, HOMO and LUMO for compounds 2, 3 and 4, respectively. In compound 1 (reported in Ref. [8]) the HOMO-1 belongs to the e″ irreducible representation, the HOMO to the e′ and the LUMO to the e″. In compound 2 the HOMO-1 belongs to the a_1', the HOMO to the e″ and the LUMO to the a_1'. In compound 3 the HOMO-1 belongs to the e′ irreducible representation, the HOMO to the e″ and the LUMO to the a′. Finally, in compound 4 the HOMO-1 belongs to the e″, the HOMO to the e′ and the LUMO to the e″ irreducible representation. In synthesis, the frontier orbitals of compounds 1 and 4 show similar symmetry, which is different for compounds 2 and 3, that are similar between them. In Table 3 the energy of the selected orbitals is reported. As can be seen, the HOMO for compound 2 is almost degenerated with HOMO-1. The orbitals are mainly in the five member rings, indicating an electronic delocalization, with contributions from the d orbitals of the gold atoms. The LUMO is localized at the center of the molecule and it includes d contribution of the gold atoms. The shape of the LUMOs is indicative of aromaticity in the inner ring.

The molecular orbitals of compounds 3 and 4 are quite similar. Both show a strong participation of the gold d orbitals, and the electronic delocalization of the side rings is at the
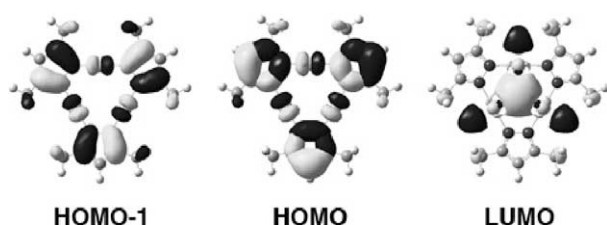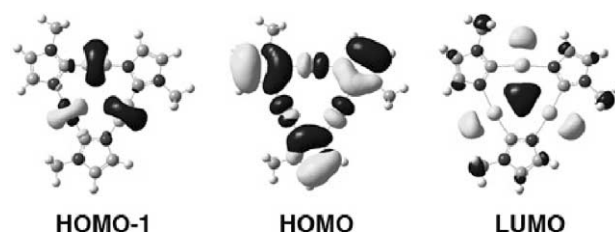

Fig. 3. Spatial representation of HOMO-1, HOMO and LUMO of compound 3.

HOMO and HOMO-1 of compounds 3 and 4, respectively. HOMO for compound 2 is similar to HOMO of compound 3 and HOMO-1 of compound 4. For all these orbitals, the d orbitals of the gold atoms produce an antibonding orbital with the π orbitals of the rings.

NICS values at the center of the rings were calculated and reported in Table 4. These results should be considered with care because the NICS technique is very sensitive with respect to the basis. In this case there is a mixing of basis with pseudopotential for Au atoms. The biggest values are for the five-member ring of compounds 2 and 3. An electronic delocalization phenomenon as aromaticity is present in the rings of the four molecules. For compounds with only Au atoms, similar electronic currents were reported previously [26]. However, the complexes of Fig. 1 show the metal atoms sharing the ring current with carbon and nitrogen. The presence of this characteristic is due to the nature of the molecular orbitals HOMO and LUMO. In these orbitals, the atomic orbitals of the Au atoms interact with p_z orbitals of carbon and nitrogen, giving place to π clouds in a similar fashion that in benzene.

Oxidation of these compounds to give Au(III) atoms should destroy the aromaticity in the nine-member ring. Thus, oxidation of 1 should be easier than that of the other compounds. The aromaticity on the side rings may induce that some aromatic character is retained after the first oxidation. Since compound 3 is less aromatic in the nine member ring than 2, it should be easier to oxidize. Some of the aromatic character of the inner ring can be transferred to the side rings. On this basis it can be expected that compound 4 should be more difficult to oxidize than 2 and 3.

The oxidation can also be related with the HOMO energy. As can be seen in Table 3, the smallest value is for compound 3 and as a consequence it should be easier to oxidize. This is in agreement with the conclusion from the aromatic character.

The presences of aromaticity change the behavior of these molecules with respect to other organometallic Au compounds.

Fig. 2. Spatial representation of HOMO-1, HOMO and LUMO of compound 2.

Fig. 4. Spatial representation of HOMO-1, HOMO and LUMO of compound 4.

Table 3
Energies and symmetries of the frontier orbitals in eV

Compound	1		2		3		4	
HOMO-1	−6.61	e''	−6.173	a'_1	−6.17	e'	−6.76	e''
HOMO	−6.31	e'	−6.169	e''	−5.88	e''	−6.00	e'
LUMO	−0.67	e''	−0.41	a'_1	−0.33	a'	−1.42	e''
GAP	5.64		5.76		5.55		4.58	

First, the great stability of these compounds, besides the compromise of the electrons in a ring current, avoids the low electronic energy interchange with other substances. Therefore, the oxidation is very difficult and the intra-molecular movements are favored as in luminescent phenomena. Second, the aromatic clouds can interact among them or with other metal centers. This characteristic added to the aurophilicity, favors the staking of several molecules as it has been observed in X-Ray analysis. The aromatic behavior may give rise to the appearance of the mesophases in compound **2**.

NBO results for some selected atoms are reported in Table 5. As can be seen, nitrogen atoms are negative while the gold atoms are positive. There is a charge transfer process from the nitrogen to the gold(I). The charge of the carbon atoms is smaller than the charge of the N for all compounds. The atomic charges contribute to the bond, since there are some electrostatic interactions between gold and nitrogen atoms. It is possible to find a correlation between the atomic charge and the bond lengths, namely, larger the atomic charge of the gold atom, shorter the Au–N bond distance.

4. Conclusions

The optimized structures are in good agreement with the available experimental results. Calculation of the electronic structure show that compounds **2** and **4** should have similar properties, while compounds **1** and **4** should be different. The three compounds show an aromatic behavior of the inner and outer rings. The great stability of these compounds due to their aromatic character, avoids the low energy electronic interchange with other substances. Aromaticity should play an important role in the properties of these three compounds, particularly in the appearance of the columnar mesophase of compound **2**.

Table 4
NICS calculated at the center of the rings

Compound	1	2	3	4
Nine member ring	−12.3	−10.1	−8.9	−10.9
Five or six member rings		−17.1	−18.3	−10.2

Table 5
NBO charge analysis of atoms inner the ring

Compound	1	2	3	4
Au	0.41	0.51	0.43	0.43
N	−0.67	−0.42	−0.65	−0.58
C	0.28		0.08	−0.07

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