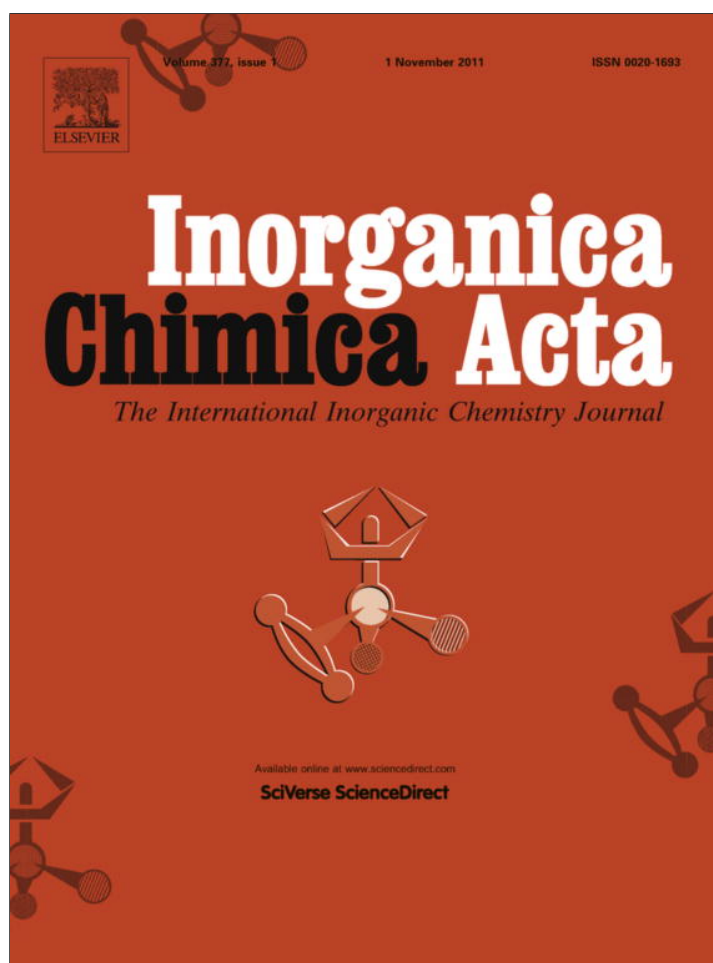


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## Aurophilic interaction in gold(I) thiosaccharinates: Synthesis, characterization, crystal structures and DFT theoretical study

Mariana Dennehy<sup>a,\*</sup>, Oscar V. Quinzani<sup>a,1</sup>, Ricardo M. Ferullo<sup>a,b</sup>, Alejandro Granados<sup>c</sup>, Robert A. Burrow<sup>d</sup>

<sup>a</sup> INQUISUR, Departamento de Química, Universidad Nacional del Sur, Avda. Alem 1253, B8000CPB Bahía Blanca, Argentina

<sup>b</sup> Departamento de Física, Universidad Nacional del Sur, Avda. Alem 1253, B8000CPB Bahía Blanca, Argentina

<sup>c</sup> INFIQC, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, C.P. 5000, Córdoba, Argentina

<sup>d</sup> Laboratório de Materiais Inorgânicos, Departamento de Química, Universidade Federal de Santa Maria, 97105-900 Santa Maria, RS, Brazil

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### ABSTRACT

The reaction of gold with thiosaccharin ligand and additional phosphorous coligands is studied. Four new Au(I) complexes with thiosaccharinate as coordinating counteranion: [Au(tsac)(PPh<sub>3</sub>)], [Au<sub>2</sub>(tsac)<sub>2</sub>(dppm)]·EtOH, Au<sub>2</sub>(tsac)<sub>2</sub>(dppe)·EtOH, and Au(tsac)(Htsac)·0.25 EtOH (tsac: thiosaccharinate, C<sub>6</sub>H<sub>4</sub>C(S)NSO<sub>2</sub><sup>-</sup>, dppm: bis(diphenylphosphino)methane, dppe: bis(diphenylphosphino)ethane) were synthesized and characterized by means of spectroscopic techniques (IR, UV–Vis, and <sup>1</sup>H, <sup>13</sup>C and <sup>13</sup>P NMR). The crystal structure of two of them, [Au(tsac)(PPh<sub>3</sub>)] and [Au<sub>2</sub>(tsac)<sub>2</sub>(dppm)]·EtOH, were solved applying single crystal X-ray diffraction and studied using the density functional theory (DFT) formalism. In the latter, the aurophilic interaction between the two gold centers was analyzed and theoretically confirmed.

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### 1. Introduction

Numerous reports on the coordination of thiolates to gold can be found in the literature [1]. Thiolate–gold(I) complexes have been used for over 60 years for the treatment of rheumatoid arthritis and cancer and therefore they have an enormous biological interest [2]. The impact of these complexes is also due to their luminescence properties and several reports on luminescence of gold(I) thiolates exist [3]. Some works in this field take account of the coordination chemistry of thioamidates (thionates), having both S and N donor atoms, and triorganophosphino ligands to gold(I), such as complexes with pyridine-2-thione, 1H-pyrimidine-2-thione, 4,6-dimethylpyrimidine-2-thione (4,6-Me<sub>2</sub>pymS), quinoline-8-thione [4–6] or with similar ligands [7].

Theoretical studies on gold complexes have also undergone a huge development during the last decade [8], because of the interesting behavior of these metal complexes with characteristic short range Au···Au contacts (2.8–3.5 Å) for which bonding can still be considered, showing the now widely accepted “aurophilic” phenomenon. These contacts are in the range of a weak bonding, and it is generally accepted that they have strength comparable to the hydrogen bonding. Theoretical aspects of the gold–phosphine–thiolate systems have been studied and reported. The theoretical

calculations yielded good agreement with the observed crystal structures and the gold–gold interaction has been confirmed [9].

The sac anion (deprotonated form of Hsac, also named 1,1-dioxo-1,2-benzothiazol-3-one or o-benzosulfimide) has several potential donor atoms such as an imino nitrogen, a carbonyl and two sulfonyl oxygen atoms, which enable the monoanion to behave as mono-, bi- or tridentate ligand [10]. Thiosaccharine, the thione form of saccharin, as it is well-known for other heterocyclic thiones, has a tautomeric equilibrium in solution and in its thiolate form can act as a good coordinating agent for soft metals, hence giving rise to mononuclear and poly-nuclear structures with or without the presence of other ligands. It is a fascinating and versatile ligand, capable of coordinating in many different modes to metals [11]. We have been investigating its coordination to the d<sup>10</sup> Cu(I) [12] and Ag(I) [13] coinage metals. Due to the very interesting results obtained on solid thiosaccharinates, and also in their potential applications in different fields as pharmaceuticals, we decided to extend these studies to gold(I). Herein we report the synthesis and the spectroscopic study and the crystal structure analysis of gold thiosaccharinate and ternary gold thiosaccharinates with organophosphino coligands: [Au(tsac)(PPh<sub>3</sub>)], [Au<sub>2</sub>(tsac)<sub>2</sub>(dppm)]·EtOH, Au<sub>2</sub>(tsac)<sub>2</sub>(dppe)·EtOH, and Au(tsac)(Htsac) (tsac: thiosaccharinate, C<sub>6</sub>H<sub>4</sub>C(S)NSO<sub>2</sub><sup>-</sup>, dppm: bis(diphenylphosphino)methane, dppe: bis(diphenylphosphino)ethane). The crystal structure analysis and the theoretical structural optimization of [Au(tsac)(PPh<sub>3</sub>)] and [Au<sub>2</sub>(tsac)<sub>2</sub>(dppm)] is presented. The analysis

\* Corresponding author.

E-mail address: [mdennehy@uns.edu.ar](mailto:mdennehy@uns.edu.ar) (M. Dennehy).

<sup>1</sup> Deceased author.

of the aurophilic interaction in the latter compound is also informed.

## 2. Experimental

### 2.1. General remarks

All chemicals were of analytical reagent grade and used as purchased. The solvents used were of analytical reagent grade and dried by commonly used techniques [14]. Solid thiosaccharin (Htsac) in its  $\alpha$ -form was prepared and characterized as previously reported [15]. The elemental analysis of C, H, and N were performed with a Thermo ElectronFlashEA 1112 Elemental Analyzer at UMYMFOR (FCEyN, UBA, Argentina) and were found to be in good agreement with the calculated values. The IR spectra of the substances were recorded as KBr pellets and Nujol mulls in the 4000–400  $\text{cm}^{-1}$  range on a Nicolet Nexus FTIR spectrometer. The UV–Vis spectra of the solids (dispersed in KBr) were registered using a Cecil 2021 spectrophotometer. The  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra of solutions of the substances were recorded on a Bruker Avance II NMR 400 MHz in  $\text{DMSO}-d_6$  using the residual peak of solvent as internal reference and 85%  $\text{H}_3\text{PO}_4$  as internal and external references, respectively.

### 2.2. Crystallography

Crystal data, data collection procedure, structure determination and refinement methods results for the two compounds are summarized in Table 1.

Data Collection: Bruker APEX2/BIS/COSMO (Bruker, 2006); cell refinement: Bruker SAINT (Bruker, 2006); data reduction: Bruker SAINT/SADABS/XPREP (Bruker, 2004, 2005, 2006). Programs used to solve and refine structure: SHELXTL (Bruker, 2001); molecular graphics: Crystal Impact Diamond 3 (Bradenburg).

### 2.3. Theoretical calculations

Density functional theory (DFT) quantum-mechanical calculations were used to optimize the geometry of  $[\text{Au}(\text{tsac})(\text{PPh}_3)]$  and  $[\text{Au}_2(\text{tsac})_2\text{dppm}]$  complexes. The gradient corrected Becke's three parameters hybrid exchange function in combination with the correlation function of Lee, Yang and Parr (B3LYP) as implemented in the software package GAUSSIAN09 [16] was used. Geometry optimization procedures were started from the experimental crystallographic data of both complexes employing the 6-31G\*\* basis sets for C, H, S, N, and O atoms. For Au, the Los Alamos effective core potentials and valence basis set were used (LANL2DZ). Our numerical accuracy for the calculation of distances and angles is in the order of thousandth of Å and hundredth of degrees, respectively.

### 2.4. Syntheses of the gold complexes

#### 2.4.1. $[\text{Au}(\text{tsac})(\text{PPh}_3)]$ (1)

2.4.1.1. (1,1-Dioxide-1,2-benzisothiazol-3-thionato- $\kappa\text{S}$ )triphenylphosphinegold(I). A solution of  $\text{PPh}_3$  (42 mg, 0.16 mmol) in ethanol (10 mL) was warmed at 45 °C. A yellow solution of  $\text{AuCl}_3$  (25 mg, 0.082 mmol) in ethanol (5 mL) was added dropwise to the initial warm solution with mechanical stirring. This solution was kept at 45 °C until it was totally decolorized. To that colorless solution, another solution of Htsac (16.4 mg, 0.082 mmol) in 5 mL of ethanol was added. The obtained clear yellow solution produced very thin pale yellow needles, suitable for X-ray diffraction study, after 7 days of slow evaporation of the solvent. Only the first batch of crystals was separated and washed with diethylether. Yield: 13 mg,

**Table 1**

Crystal data and structure refinement for  $[\text{Au}(\text{tsac})(\text{PPh}_3)]$  (1) and  $[\text{Au}_2(\text{tsac})_2(\text{dppm})]\cdot\text{EtOH}$  (2) complexes.

	1	2
Empirical formula	$\text{C}_{25}\text{H}_{19}\text{AuNO}_2\text{PS}_2$	$\text{C}_{41}\text{H}_{36}\text{Au}_2\text{NO}_5\text{P}_2\text{S}_4$
Formula weight	657.47	1220.83
$T$ (K)	100(2)	100(2)
$\lambda$ (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/c$
Unit cell dimensions		
$a$ (Å)	19.7402(13)	15.993(3)
$b$ (Å)	13.5528(9)	18.046(3)
$c$ (Å)	17.5357(8)	14.510(3)
$\alpha$ (°)	90	90
$\beta$ (°)	101.309(2)	100.617(7)
$\gamma$ (°)	90	90
$V$ (Å <sup>3</sup> )	4600.3(5)	4116.1(13)
$Z$	8	4
$D_{\text{calc}}$ (mg/m <sup>3</sup> )	1.899	1.970
Absorption coefficient (mm <sup>-1</sup> )	6.670	7.448
$F(0\ 0\ 0)$	2544	2352
Crystal size (mm)	$0.21 \times 0.09 \times 0.08$	$0.25 \times 0.19 \times 0.04$
$\theta$ (°)	2.07–30.52	2.08–30.41
Index ranges	$-27 \leq h \leq 28$ $-16 \leq k \leq 19$ $-25 \leq l \leq 24$	$-22 \leq h \leq 22$ $-24 \leq k \leq 25$ $-20 \leq l \leq 20$
Reflections collected	25 902	47 373
Independent reflections ( $R_{\text{int}}$ )	7013 (0.0532)	12 410 (0.0691)
Completeness to $\theta$	30.52° 99.7%	30.41° 99.5%
Absorption correction	GAUSSIAN	
Maximum and minimum transmission	0.7461 and 0.6217	0.7730 and 0.3861
Refinement method	Full-matrix least-squares on $F^2$	
Data/restraints/parameters	7013/0/289	12 410/0/515
Goodness-of-fit (GOF) on $F^2$	0.996	1.015
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0340$ , $wR_2 = 0.0591$	$R_1 = 0.0399$ , $wR_2 = 0.0781$
$R$ indices (all data)	$R_1 = 0.0542$ , $wR_2 = 0.0655$	$R_1 = 0.0830$ , $wR_2 = 0.0928$
Largest difference peak and hole (e Å <sup>-3</sup> )	1.227 and -0.843	1.780 and -2.467

$R$ -indices defined as:  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ .

25%. Anal. Calc. for  $\text{C}_{25}\text{H}_{19}\text{AuNO}_2\text{PS}_2$ : C, 45.7; H, 2.9; N, 2.1. Found: C, 45.7; H, 2.8; N, 2.2%.

#### 2.4.2. $[\text{Au}_2(\text{tsac})_2\text{dppm}]\cdot\text{EtOH}$ (2)

2.4.2.1.  $\mu$ -Bis(diphenylphosphino)methane- $\kappa\text{P},\text{P}'$ -bis[(1,1-dioxide-1,2-benzisothiazol-3-thionato- $\kappa\text{S}$ )gold(I)] solvato ethanol. A yellow solution of  $\text{AuCl}_3$  in ethanol (25 mg, 0.082 mmol, 5 mL) was dropwise added to a warm ethanolic solution of dppm (31 mg, 0.081 mmol, 45 °C). The resulting yellow solution was kept under mechanical stirring until decolorized. A solution of Htsac (16.4 mg, 0.082 mmol, 5 mL EtOH) was added to the later. A clear yellow solution was obtained. Yellow crystals, suitable for X-ray structural analysis, were obtained after 24 h of slow evaporation of the solvent. They were washed with diethylether and air dried. Only the first batch of crystals was analyzed. Yield: 9 mg, 34%. Anal. Calc. for  $\text{C}_{41}\text{H}_{36}\text{Au}_2\text{N}_2\text{O}_5\text{P}_2\text{S}_4$ : C, 40.3; H, 3.0; N, 2.3. Found: C, 40.4; H, 3.0; N, 2.3%.

#### 2.4.3. $\text{Au}_2(\text{tsac})_2\text{dppe}\cdot\text{EtOH}$ (3)

The substance was prepared following the same procedure as for complex 2 using dppe (32 mg, 0.082 mmol) instead of dppm. A very pale yellow microcrystalline product was obtained by slow evaporation of the solvent. The first batch was separated and washed with diethylether. The efforts to obtain single crystals of this complex so far have been useless. Yield: 9 mg, 34%. Anal. Calc. for  $\text{C}_{42}\text{H}_{38}\text{Au}_2\text{N}_2\text{O}_5\text{P}_2\text{S}_4$ : C, 40.9; H, 3.1; N, 2.3. Found: C, 41.4; H, 3.1; N, 2.3%.

#### 2.4.4. $\text{Au}(\text{tsac})(\text{Htsac})_2 \cdot 0.25 \text{EtOH}$ (**4**)

$\text{AuCl}_3$  (50 mg, 0.16 mmol) was decomposed in air steam at 185 °C, following the technique proposed by Thomsen [17]. The obtained product,  $\text{AuCl}$ , was dissolved in ethanol (5 mL), resulting in a clear yellow solution. A solution of Htsac in ethanol (98 mg, 0.49 mmol, 5 mL) was slowly added with constant mechanical stirring. After 5 min a yellow precipitate appeared, which was filtered, washed with diethylether and air dried. Yield: 30 mg, 23%. *Anal.* Calc. for  $\text{C}_{21.5}\text{H}_{15.5}\text{AuN}_3\text{O}_{6.25}\text{S}_6$ : C, 32.2, N, 5.2, H, 1.7. Found: C, 32.3; N, 5.5; H, 2.2%.

When the direct reaction of Htsac and  $\text{AuCl}_3$  was held with the intention to obtain the binary gold(III) thiosaccharinate, the reduction of the metal to Au(I) with concomitant formation of the thiosaccharine disulfide,  $(\text{tsac})_2$ , was observed. The last product was also obtained during the synthesis of the  $[\text{Cu}_4(\text{tsac})_4(\text{CH}_3\text{CN})_2] \cdot 2\text{CH}_3\text{CN}$  complex [11] with  $\text{Cu}(\text{CH}_3\text{COO})_2$  and Htsac as starting reactants, as the result of the reduction of Cu(II) to Cu(I).

### 3. Results and discussion

#### 3.1. Crystal structures

##### 3.1.1. $[\text{Au}(\text{tsac})(\text{PPh}_3)]$ (**1**)

A molecular plot of this mononuclear complex is shown in Fig. 1. Selected bond distances and angles are listed in Table 2. Within the molecule, the gold atom is coordinated to the exocyclic sulfur atom of the thiosaccharinate anion ( $\text{Au}(1)-\text{S}(1)$ , 2.3168(9) Å) and to the phosphorous atom of the phosphine molecule ( $\text{Au}(1)-\text{P}(1)$ , 2.2623(9) Å) in a linear configuration. Pairs of these molecules (Fig. 2) are associated intermolecularly via weak auriphilic Au–Au contact ( $\text{Au}-\text{Au}$  bond distance: 3.440 Å). In the cell structure, the

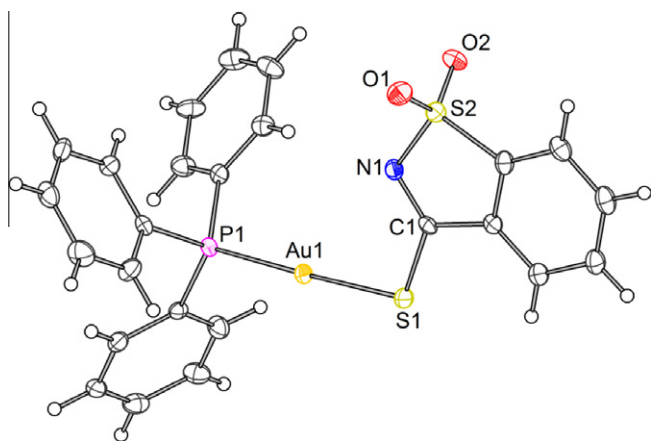


Fig. 1. Molecular drawing of  $[\text{Au}(\text{tsac})(\text{PPh}_3)]$  with 50% probability ellipsoids.

Table 2

Selected bond lengths (Å) and angles (°) for  $[\text{Au}(\text{tsac})(\text{PPh}_3)]$ .

	Experimental	Calculated
$\text{Au}(1)-\text{P}(1)$	2.2623(9)	2.341
$\text{Au}(1)-\text{S}(1)$	2.3168(9)	2.407
$\text{C}(1)-\text{N}(1)$	1.315(5)	1.305
$\text{C}(1)-\text{S}(1)$	1.713(4)	1.741
$\text{N}(1)-\text{S}(2)$	1.665(3)	1.706
$\text{C}(11)-\text{P}(1)$	1.807(4)	1.832
$\text{C}(21)-\text{P}(1)$	1.814(4)	1.834
$\text{C}(31)-\text{P}(1)$	1.822(3)	1.834
$\text{P}(1)-\text{Au}(1)-\text{S}(1)$	176.53(3)	172.10
$\text{Au}(1)-\text{S}(1)-\text{C}(1)$	104.69(13)	98.03
$\text{N}(1)-\text{C}(1)-\text{S}(1)$	126.1(3)	123.81

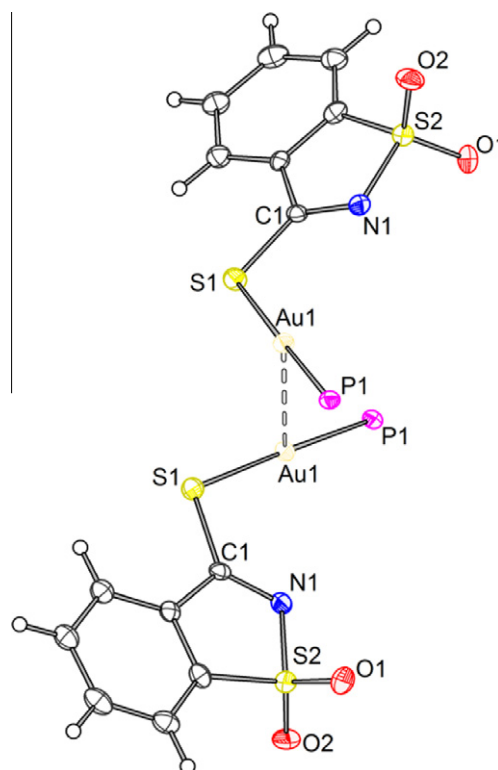


Fig. 2. Molecular drawing of two molecular units of  $[\text{Au}(\text{tsac})(\text{PPh}_3)]$ , showing the twisted angle towards the closer gold atom with 50% probability ellipsoids. Phenyl rings and hydrogen atoms are omitted for clarity.

$\text{P}-\text{Au}-\text{S}$  angles are found to deviate from linearity ( $176.53(3)^\circ$ ) thus facilitating the mutual approach of the metal atoms (Fig. 2). This displacement has been observed and reported previously for other mononuclear linear gold(I) complexes  $\text{L}-\text{Au}-\text{X}$  [8e]. The structure of this thiosaccharinate can be compared with the quite similar gold–thionate complex  $[\text{Au}(4,6\text{-Me}_2\text{pymS})(\text{PPh}_3)]$  [5] (4,6-Me<sub>2</sub>-pymS: 4,6-dimethylpyrimidine-2-thiolato) with bond distances of  $\text{Au}-\text{P} = 2.247(2)$  Å,  $\text{Au}-\text{S} = 2.289(2)$  Å and an angle of  $\text{P}-\text{Au}-\text{S} = 178.19(11)^\circ$ , and the  $(\text{Ph}_3\text{P})\text{AuSPh}(o\text{-Cl})$  complex reported by Forward et al. [18]; this latter compound has also a linear geometry and similar  $\text{Au}-\text{P}$  and  $\text{Au}-\text{S}$  bond distances ( $\text{Au}(1)-\text{P}(1)$ , 2.255(2) Å and  $\text{Au}(1)-\text{S}(1)$ , 2.292(2) Å). Within the thiosaccharinate anion, the distances of the thioamidate group reflects the strong coordination of the exocyclic sulfur atom to the gold center. While the  $\text{C}1-\text{S}1$  distance is longer than the corresponding one at “free” thiosaccharinate [19] found for the  $\text{PNP}(\text{tsac})$  (1.713(4) versus 1.678(2) Å), the  $\text{C}1-\text{N}1$  distance is shortened (1.315(5) versus 1.324(3) Å).

##### 3.1.2. $[\text{Au}_2(\text{tsac})_2(\text{dppm})] \cdot \text{EtOH}$ (**2**)

Fig. 3 shows a molecular plot of the structure of complex **2**. Some selected geometrical parameters (bond distances and angles) are presented in Table 3.

Each of the two gold(I) centers are linearly coordinated to one exocyclic sulfur atom from a thiosaccharinate and to a phosphorous atom from the diphosphine molecule, which acts as a bridge between the two metal atoms. The short distance between the two gold atoms,  $d(\text{Au}-\text{Au}) = 3.1686(6)$  Å, allows stating the existence of auriphilic interaction in this complex. The anions are monocoordinated to the metal trough their exocyclic S atoms. This compound can be compared to the  $[\text{Au}_2(p\text{-tc})_2(\text{dppm})]$  complex [20] (*p*-tc: *p*-thiocresol) which has a gold–gold bond distance of 3.200(1) Å,  $\text{Au}-\text{P}$  bond distances of 2.265(3) and 2.272(2) Å, and  $\text{Au}-\text{S}$  bond distances of 2.313(3) and 2.310(3) Å, similar to the those found for  $[\text{Ag}_2(\text{tsac})_2(\text{dppm})] \cdot \text{Et}(\text{OH})$ . This gold thiosaccharinate has weak

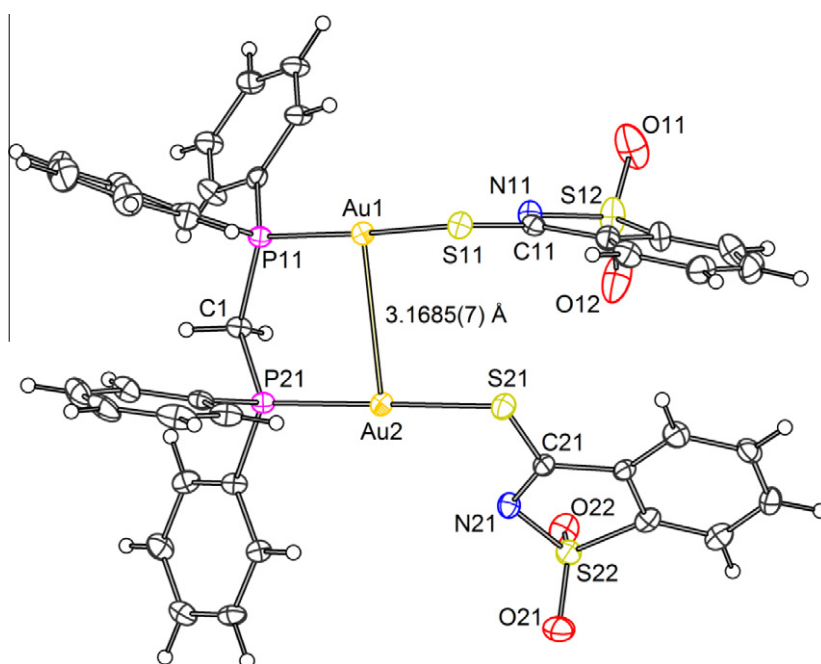


Fig. 3. Molecular drawing of  $[\text{Au}_2(\text{tsac})_2(\text{dppm})]$  with 50% probability ellipsoids.

Table 3  
Selected bond distances (Å) and angles (°) for  $[\text{Au}_2(\text{tsac})_2(\text{dppm})]\cdot\text{EtOH}$ .

	Experimental	Calculated
Au(1)–Au(2)	3.1686(6)	3.360
C(21)–N(21)	1.315(7)	1.306
C(11)–N(11)	1.298(6)	1.306
Au(2)–S(21)	2.3250(16)	2.404
Au(1)–S(11)	2.3176(15)	2.405
Au(1)–P(11)	2.2621(15)	2.347
Au(2)–P(21)	2.2677(16)	2.345
C(21)–S(21)	1.723(6)	1.740
C(11)–S(11)	1.719(6)	1.740
P(11)–Au(1)–S(11)	173.36(5)	169.94
P(21)–Au(2)–S(21)	179.57(5)	169.80
Au(1)–S(11)–C(11)	102.80(19)	97.55
Au(2)–S(21)–C(21)	105.3(2)	97.88
N(21)–C(21)–S(21)	124.6(5)	123.75

Table 4  
Hydrogen bonds (Å and °) for  $[\text{Au}_2(\text{tsac})_2(\text{dppm})]\cdot\text{EtOH}$ .

D–H...A	d(D–H)	d(H...A)	d(D...A)	∠(DHA)
O(1S)–H(1S)...O(11)#1	0.84	2.46	3.132(15)	138.3
O(1SB)–H(1SB)...O(21)#2	0.84	1.91	2.748(14)	177.4

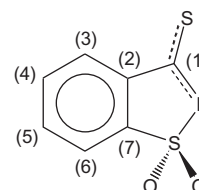
Symmetry transformations used to generate equivalent atoms: #1  $-x, -y+1, -z+1$ ; #2  $x, y, z+1$ .

hydrogen bonds between the OH hydrogen from the solvent molecule and an oxygen atom from a sulfonyl group (Table 4).

### 3.1.3. $^1\text{H}$ , $^{13}\text{C}$ and $^{31}\text{P}$ NMR spectral studies

The NMR spectra of the new complexes, in  $\text{DMSO}-d_6$  solutions, were studied and compared to the NMR responses of other metal thiosaccharinates with mono and diphosphines. The numbering scheme of the anion is shown in Scheme 1.

In the  $^1\text{H}$  NMR spectra of  $[\text{Au}(\text{tsac})(\text{PPh}_3)]$  complex (1), the signals due to the triphenylphosphine molecules lie in the range 7.52–7.75 ppm (m, 15H). Between 7.79 and 8.04 ppm, three



Scheme 1. Atoms numbering for the NMR signals assignments.

multiplets of the thiosaccharinate-proton signals appear: 7.79–7.90 (m, 2H, H4/H5), 7.94–7.97 (m, 1H, H3) and 7.97–8.04 (m, 1H, H6) ppm. They can be compared with the proton signals of thiosaccharinate monocoordinated to a silver(I) nucleus in  $[\text{Ag}(\text{tsac})(\text{PPh}_3)_2]$  [13b]. In the  $^{31}\text{P}\{^1\text{H}\}$  spectra of complex 1 only a broad singlet at 36.50 ppm is observed, downfield shifted from the free ligand. It appears at a very similar chemical shift as the reported resonance of the P atom in the complex  $[\text{Au}(\text{PPh}_3)(p\text{-tc})]$  (39.2 ppm) in which a  $\text{PPh}_3$  molecule coordinates to a gold(I) atom [20]. It indicates that  $\text{PPh}_3$  strongly coordinates to the gold atom in complex 1 and there is only one species in the  $\text{DMSO}-d_6$  solution. In the  $^{13}\text{C}$  NMR spectra of complex 1 the five signals at 121.2, 125.2, 132.3, 138.2 and 185.0 ppm can be assigned to carbon atoms resonances of the thiosaccharinate ligands [19]. The last signal, corresponding to the thiocarbonilic carbon atom (C1), is downfield shifted from the free ligand, indicating that the anion is monocoordinated to the metal through the  $\text{S}_{\text{exo}}$  center in solution [13b]. The  $\text{PPh}_3$ -carbon signals lie in the range 128.5–134.7 ppm, mixed with the resting two resonances of the thiosaccharinate anions.

The presence of only one set of signals for  $[\text{Au}_2(\text{tsac})_2(\text{dppm})]$  (2) confirms the existence of only one molecular species in  $\text{DMSO}-d_6$  solutions. In the  $^1\text{H}$  NMR the resonances of the thiosaccharinates appear as one doublet at 7.97 ppm (d, 2H, H6) and one multiplet at 7.85–7.70 ppm (m, 6H, H3/H4/H5), the last partially superimposed with a dppm multiplet. A similar spectra was obtained for a Pd(II) thiosaccharinate,  $[\text{Pd}(\text{tsac})_2(\text{dppm})]$ , with the anions tightly bonded to the metal center [21]. The presence of the ethanol molecule was also confirmed by its proton resonances

at 3.55 (q, 2H) and 1.06 (t, 3H) ppm. In the  $^{13}\text{C}$  spectra, the chemical shift (185.9 ppm) of the C(1) resonance is particularly indicative of the coordination of the anion to gold(I). The NMR spectra of  $[\text{Au}_2(\text{tsac})_2(\text{dppm})]$  then corroborate the coordination of the thiosaccharinates and the diphosphine ligands to the metals in solution. It seems that the molecular species in solution could be the dinuclear unit of the solid substance, as was reported also for the  $[\text{Au}_2(p\text{-tc})_2(\text{dppm})]$  complex [20].

The  $^1\text{H}$  NMR spectra of the complex  $\text{Au}_2(\text{tsac})_2\text{dppe}\cdot\text{EtOH}$  (**3**) in  $\text{DMSO}-d_6$  solutions show four multiplets in the region of aromatic hydrogen resonances (7.40–8.00 ppm), the expected signals for the  $\text{CH}_2$  groups of the dppe molecule (3.00–3.20 ppm) and the solvent ethanol molecule (3.44 and 1.06 ppm). The tsac-H6 resonances lie under a multiplet signal of the dppe molecule. The  $^{13}\text{C}$  spectra show many signals of the dppe molecule but only one set for the thiosaccharinate anion, with the tsac-C1 resonance at 184.0 ppm. The existence of one set of signals for the anions indicates that they are equivalent and tightly bonded to the metal centers. The  $^{31}\text{P}$  NMR spectra records only one signal, at 32.08 ppm, that was assigned to the resonances of the phosphorous atoms of the diphosphine. This value is very close to the reported value of 36.9 ppm for the  $[\text{Au}_2(p\text{-tc})_2(\text{dppe})]$  complex [20] with a very close structure as the supposed structure for the  $[\text{Au}_2(\text{tsac})_2\text{dppe}]$  complex.

In  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of  $\text{Au}(\text{tsac})(\text{Htsac})_2\cdot 0.25 \text{EtOH}$  (**4**) clearly show the presence of both the neutral and the anionic thiosaccharine in the complex. The aromatic protons resonances of both species appeared partially superimposed and are tentatively assigned. A doublet signal at 8.17 ppm corresponds to neutral thiosaccharin [22]. The thioamidic proton of the neutral thiosaccharine (H1) shows a very broad and extended signal centered at 5.78 ppm, which corresponds to the thiol form of the thiosaccharine [19]. All the carbon resonances (14) of the Htsac molecules and tsac anions were identified. In particular, the C(1) signals appearing at 182 and 161 ppm correspond to thiosaccharinates monocoordinated by the exocyclic sulfur atom [11,13], and neutral thiosaccharin [22], respectively.

### 3.2. Vibrational and electronic spectra

The spectra of the four complexes were recorded in KBr dispersions. All the bands due to the ligands were present and some intense bands due to the phosphines masked some weaker bands of the thionate. The IR spectrum of  $\text{Au}(\text{tsac})(\text{Htsac})_2\cdot 0.25 \text{EtOH}$  was also recorded Nujol mulls. In the Nujol mulls spectrum, a very broad band can be observed at  $3400 \text{ cm}^{-1}$  that could be attributed to the vibrational stretching mode of the N–H bonds of the Htsac molecules.

For the  $[\text{Au}(\text{tsac})(\text{PPh}_3)]$  the C– $\text{S}_{\text{exo}}$  bonds is weakened compared to those belonging to the not coordinated tsac. Also the bands corresponding to the stretching movement of the C– $\text{S}_{\text{exo}}$  bonds,  $\nu(\text{C}-\text{S}_{\text{exo}})$ , are shifted to a lower frequency ( $995 \text{ cm}^{-1}$ ) compared to that of the complex  $[\text{Ag}(\text{tsac})(\text{PPh}_3)_3]$  and  $[\text{Ag}(\text{tsac})(\text{PPh}_3)_2]$  ( $1006$  and  $1008 \text{ cm}^{-1}$ ). These observations confirm that the thiosaccharinate ligand is strongly coordinated to the gold atom. The spectra of  $[\text{Au}_2(\text{tsac})_2\text{dppm}]\cdot\text{EtOH}$  and  $[\text{Au}_2(\text{tsac})_2(\text{dppe})]\cdot\text{EtOH}$  complexes have similar features as the previously discussed spectrum for the  $[\text{Au}(\text{tsac})(\text{PPh}_3)]$  complex. A marked shift and a shoulder in the  $\nu_{\text{as}}(\text{SO}_2)$  vibrational band in the  $[\text{Au}_2(\text{tsac})_2\text{dppm}]\cdot\text{EtOH}$  spectrum (from  $1317 \text{ cm}^{-1}$  in the other three complexes to  $1307 \text{ cm}^{-1}$ ) is due to the hydrogen bonds present in this complex. For the  $\text{Au}(\text{tsac})(\text{Htsac})_2\cdot 0.25 \text{EtOH}$  complex the bands appearing at  $2920$  and  $2851 \text{ cm}^{-1}$  are assigned to the corresponding vibrations of the molecules of the ethanol solvent.

In the electronic spectra of the four complexes recorded in the solid state as KBr dispersions, the bands due to the  $\pi \rightarrow \pi^*$  transitions of the phenyl rings of the anion, and for complexes **1**, **2** and **3**,

of the phosphines molecules are observed at the higher energies. Less intense bands are also observed due to the  $\pi \rightarrow \pi^*$  transitions of the C– $\text{S}_{\text{exo}}$  group [23]. In the spectrum of the  $\text{Au}(\text{tsac})(\text{Htsac})_2$  complex the expectable duplication of bands due to the presence of both thiosaccharine species, protonated and anionic, is observed.

### 3.3. DFT calculations

In a previous work [11], we carried out quantum chemical investigations using the DFT formalism to investigate the curious structure of the  $[\text{Ag}_2(\text{tsac})_2\text{py}]$  complex (py = pyridine). With the same scope, the geometric structure of  $[\text{Au}(\text{tsac})(\text{PPh}_3)]$  and  $[\text{Au}_2(\text{tsac})_2(\text{dppm})]$  complexes were optimized and their molecular orbitals (MOs) were analyzed. The results obtained are a good reproduction of the experimentally observed structural parameters (see Tables 2 and 3). It has been demonstrated for this type of substances that the B3LYP method (with the selected basis sets) yields good agreement with the experimental geometries, overestimating sometimes the bond distances in dinuclear metal compounds. Although the DFT methods reproduce reasonably well the Au–Au interactions, other methods as MP2 or SCS-MP2 reproduce that interaction better, but the computational cost is also bigger [24].

Indeed, as it can be seen from Table 3, the Au–Au distance is slightly longer than the experimental one. This may be due to the fact that DFT methods are unable to describe properly the dispersion interactions, which are in part responsible for the metallophilic interaction. Comparing different computational methods in calculations of neutral metal–metal interactions, Truhlar and co-workers [25] observed that the B3LYP is among the DFT methods the one that provides the more reliable results. Furthermore, O'Grady and Kaltsoyannis [8d] also pointed out that in general

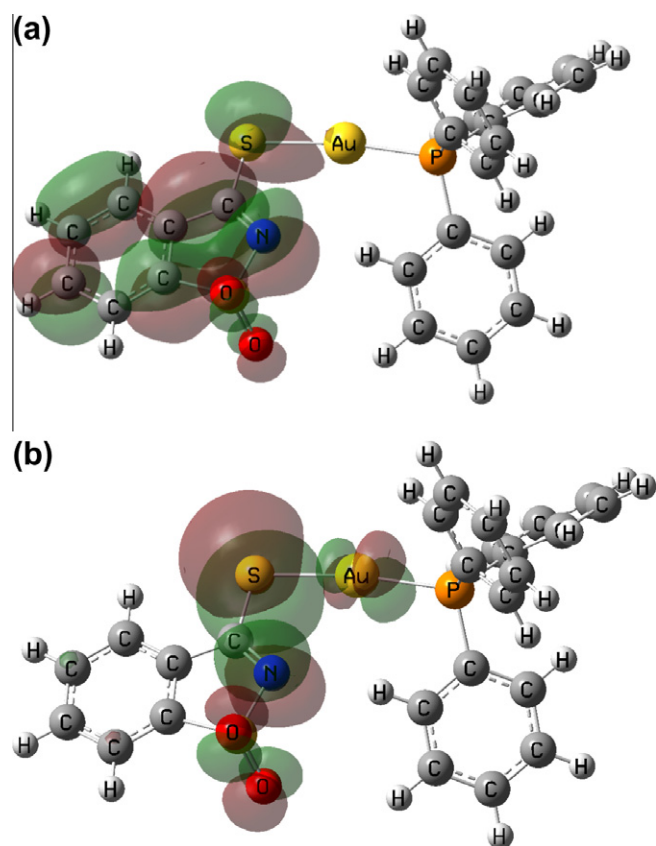


Fig. 4. Plot of (a) the LUMO and (b) the HOMO orbitals of complex  $[\text{Au}(\text{tsac})(\text{PPh}_3)]$ .

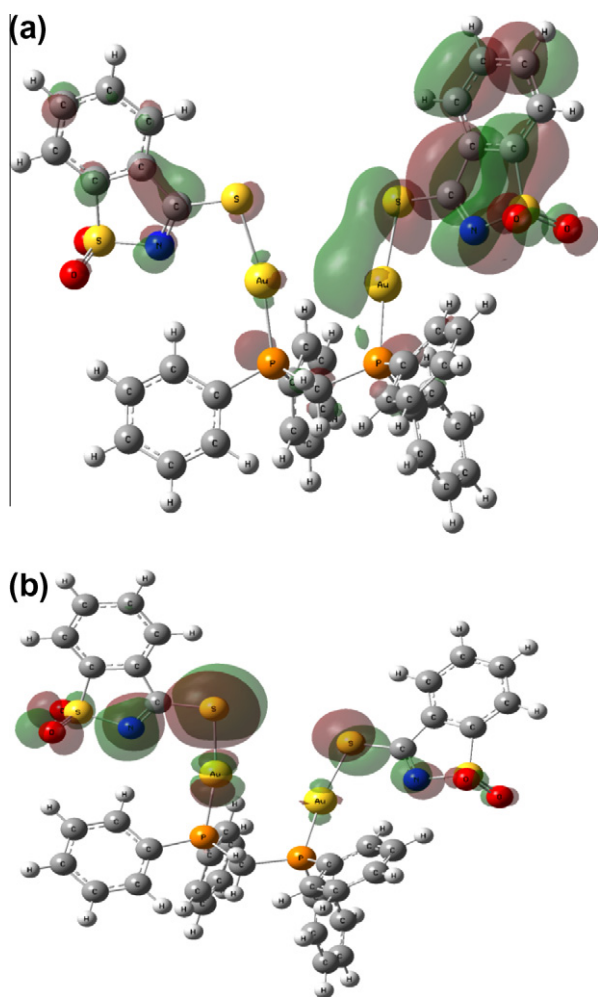


Fig. 5. Plot of (a) the LUMO and (b) the HOMO orbital of complex  $[\text{Au}_2(\text{tsac})_2(\text{dppm})]$ .

**Table 5**  
Au atom contribution percent in some selected MOs at the  $[\text{Au}_2(\text{tsac})_2(\text{dppe})]$  complex.

OM	Au1%	Au2%	Total Au%
HOMO-21	9.89	9.28	19.17
HOMO-28	38.13	32.40	70.52
HOMO-29	18.71	18.60	37.31
HOMO-30	13.94	14.03	27.97

DFT can reproduce metallophilic interactions reasonably well. In our previous work [11], we have observed the existence of MOs with high Ag–Ag bond character in the dinuclear  $[\text{Ag}_2(\text{tsac})_2\text{py}]$  complex using the DFT approach. Here, a similar study was performed for  $[\text{Au}_2(\text{tsac})_2(\text{dppm})]$ . For  $[\text{Au}(\text{tsac})(\text{PPh}_3)]$  and  $[\text{Au}_2(\text{tsac})_2(\text{dppm})]$ , the HOMOs (at  $-6.07$  and  $-6.10$  eV, respectively) and the LUMOs (at  $-1.74$  and  $-1.85$  eV, respectively) are all of  $\pi$  character and localized over thiosaccharinate anions (Figs. 4 and 5). The HOMO and LUMO orbitals of  $[\text{Au}_2(\text{tsac})_2(\text{dppm})]$  are localized over different thioamidic group. For the  $[\text{Au}_2(\text{tsac})_2(\text{dppm})]$  complex all the MOs were analyzed, searching those ones which present high contributions from Au atoms. Four MOs have Au–Au bonding character, HOMO-30, HOMO-29, HOMO-28 and HOMO-21 with high contributions of both metal centers. Table 5 shows the percent contribution of each gold atom to the MOs. The HOMO-28 is a  $\pi$ -bond with 70% of contribution of gold atoms. The above mentioned MOs are located at  $-8.95$ ,  $-8.87$ ,  $-8.68$  and  $-8.08$  eV, respectively.

#### 4. Conclusions

Four new binary and ternary gold(I) complexes are described, in which the metal atoms are coordinated by thiosaccharinate anions and by other ligands ( $\text{PPh}_3$ ,  $\text{dppm}$  and  $\text{dppe}$ ). For two of them,  $[\text{Au}(\text{tsac})(\text{PPh}_3)]$  and  $[\text{Au}_2(\text{tsac})_2(\text{dppm})]\cdot\text{EtOH}$ , the crystal structures had the expected typical structure for gold(I) thionates. The theoretical optimization of the complexes yielded good agreements between calculated and experimental geometries. The analysis performed corroborate that even if it is “ligand assisted” by the bridge of the diphosphine molecule, an aurophilic interaction is present in the  $[\text{Au}_2(\text{tsac})_2(\text{dppm})]\cdot\text{EtOH}$  complex.

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#### Appendix A. Supplementary data

Mol files, tables of experimental vibrational, NMR and electronic data are provided in the supplementary material. Calculated structural parameters of  $[\text{Au}(\text{tsac})(\text{PPh}_3)]$  and  $[\text{Au}_2(\text{tsac})_2(\text{dppm})]$  can be obtained from authors upon request. CCDC 796017 and 796018 contain the supplementary crystallographic data for  $[\text{Au}(\text{tsac})(\text{PPh}_3)]$  and  $[\text{Au}_2(\text{tsac})_2(\text{dppm})]\cdot\text{EtOH}$ , respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.07.052.

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