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Article

Gold Thione Complexes

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Abstract: The reaction of the ligand Et_4todit (4,5,6,7-Tetrathiocino-[1,2-*b*:3,4-*b*']-diimidazolyl-1,3,8,10-tetraethyl-2,9-dithione) with gold complexes leads to the dinuclear gold(I) complexes $[\{Au(C_6F_5)\}_2(Et_4todit)]$ and $[Au(Et_4todit)]_2(OTf)_2$, which do not contain any gold-gold interactions, or to the gold(III) derivative $[\{Au(C_6F_5)_3\}_2(Et_4todit)]$. The crystal structures have been established by X-ray diffraction studies and show that the gold centers coordinate to the sulfur atoms of the imidazoline-2-thione groups.

Keywords: gold(I); gold(III); imidazole derivatives

1. Introduction

The coordination chemistry of organosulfur compounds featuring two or more 3-alkylimidazole-2-thione groups has not been studied in depth in spite of their potential structural coordination possibilities. The most intensely studied ligands are the derivatives that contain two 3-methylimidazoline-2-thione groups bounded by a $–(CH_2)_n–$ chain [n = 1 (Mbit), 2 (Ebit), 4 (Bbit)] and some complexes with nickel(II), cobalt(II) [1], rhodium(III) and iridium(III) [2], antimony(III), bismuth(III) [3], tin(IV) [4], lead(II) [5], silver(I) [6,7] and group 11 elements [7] have been described in the literature with these types of ligands.

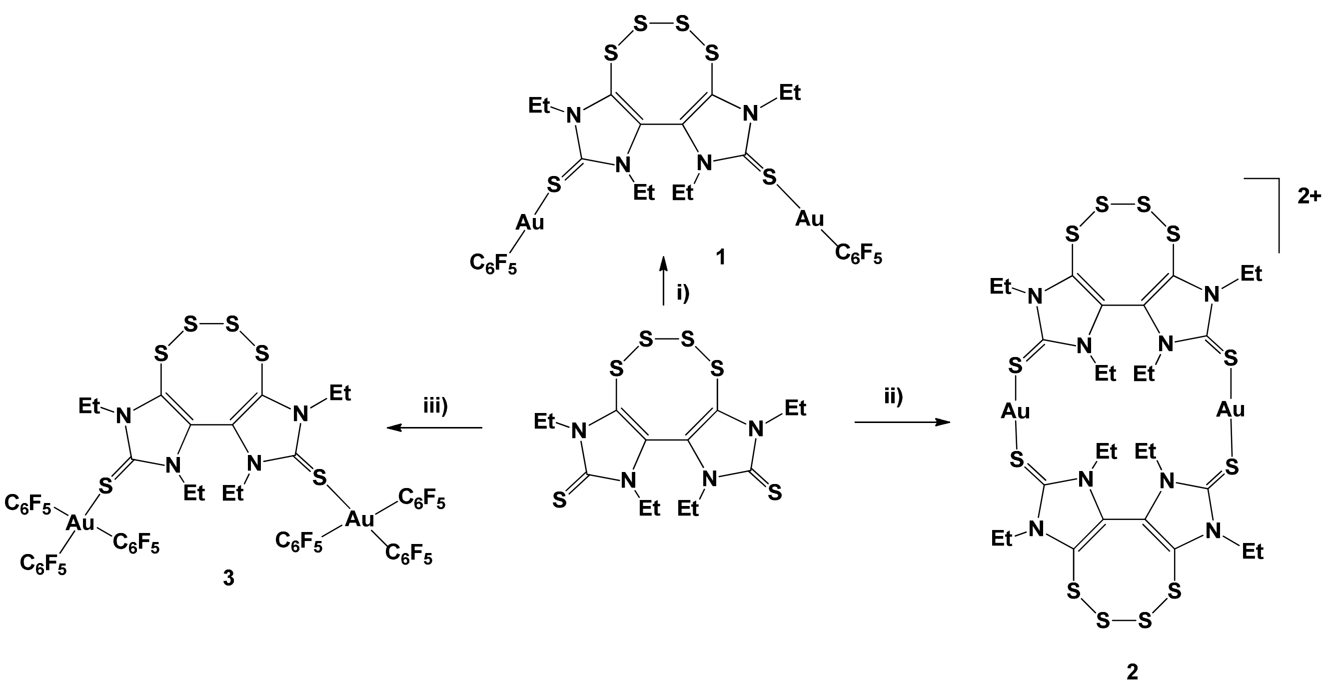
Tetrathiocino-diimidazolyl species also contains two C=S groups that can behave as donors towards Lewis acids [8–10]. In particular, the ligand Et_4todit (4,5,6,7-tetrathiocino-[1,2-*b*:3,4-*b*']-diimidazolyl-1,3,8,10-tetraethyl-2,9-dithione) (Scheme 1) features very distant positions of the thiocarbonyl groups that make this molecule capable to act as bidentate bridging ligand. Some polymeric complexes with stoichiometry [$M(Et_4todit)X_2$] (M = Zn, Cd, Hg; X = Cl, Br) [11] or [Cu(Et_4todit)I] [12] have been reported. This notwithstanding, no one gold complex with this type of ligand has been obtained to date.

In this paper we report the synthesis and structural characterization of the dinuclear gold(I) complexes [$\{Au(C_6F_5)\}_2$(Et_4todit)] and [Au(Et_4todit)]$_2$(OTf)$_2$ and of the gold(III) derivative [$\{Au(C_6F_5)_3\}_2$(Et_4todit)].

2. Results and Discussion

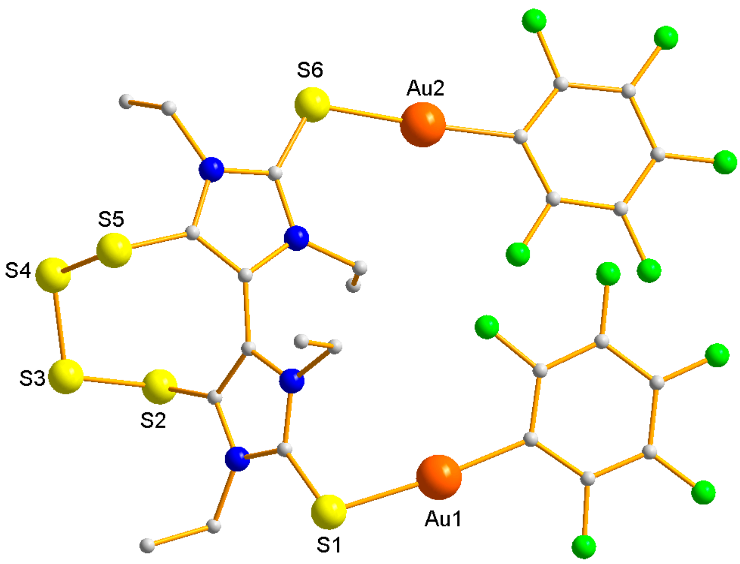
The Et_4todit ligand was prepared from the corresponding imidazoline-2-thione-4,5-dione by reaction with the Lawesson's reagent, as it was described previously [9,13,14]. The HOMO-1 and HOMO calculated at DFT level for Et_4todit are built up of the in-phase and out-of-phase combinations of the non-bonding lone pairs localized on the sulfur atoms, perpendicular to the imidazole plane, respectively, with remarkably negative NBO charges [9]. The terminal thiocarbonyl groups are potential donors not only towards molecular acids, [8–10] but also towards transition metal ions [11,12]. We have, therefore, studied the coordination properties of this ligand towards gold(I) and gold(III) derivatives. Scheme 1 represents the synthesized complexes.

Scheme 1. (**i**) 2[$Au(C_6F_5)(tht)$], (**ii**) [$Au(tht)_2$]OTf, (**iii**) 2[$Au(C_6F_5)_3(tht)$].



The reaction of Et_4todit with [Au(C_6F_5)(tht)] (tht = tetrahydrothiophene, molar ratio = 1:2) leads to the dinuclear derivative [{Au(C_6F_5)}$_2$(Et_4todit)] (**1**) (Scheme 1). It is a white solid that has been characterized by ^{1}H-NMR and ^{19}F-NMR spectroscopy and mass spectrometry. Single crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane in a solution of **1** in 1,2-dichloroethane, and the molecular structure is depicted in Figure 1. The two five-membered rings of the bis(thiocarbonyl) donors are twisted about the C–C bond by 71.19°, similarly to what found in the crystal structure of Et_4todit (69.90°) and its derivatives, such as Et_4todit·2Br_2, where the four independent molecules of the asymmetric units show torsion values ranging between 67.5° and 79.7° [9,14]. The two gold centers present a distorted linear geometry and are bonded to the C=S groups of the thioimidazol rings and to the pentafluorophenyl groups. The S(1)–Au(1)–C(1) angle (174.8(1)°) and the Au(1)–C(1) (2.022(4) Å) and Au(1)–S(1) (2.333(1) Å) bond distances found in the solid structure are in good agreement with those reported in the literature [4,5]. No Au(I)–Au(I) interactions have been observed in the crystal structure. The complex is not luminescent in solid state or in solution.

Figure 1. Molecular structure of the compound **1**, with the atom labeling scheme (hydrogen atoms omitted for clarity).



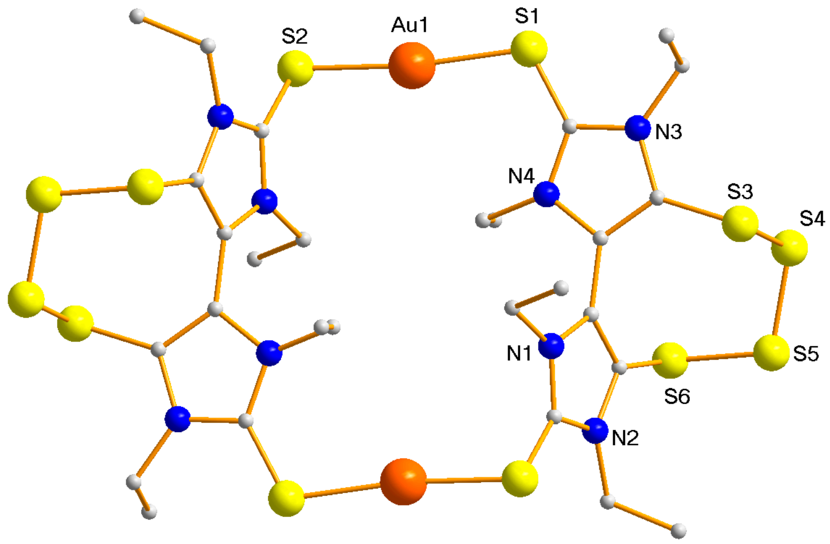
A selection of bond lengths and angles for complex **1** are summarized in Table 1.

Table 1. Selected bond lengths (Å) and angles (°) for **1**.

Distances (Å)			Angles (°)
Au(1)–S(1)	2.333(1)	S(1)–Au(1)–C(1)	174.8(1)
Au(2)–S(6)	2.309(1)	Au(1)–S(1)–C(7)	97.8(1)
Au(2)–C(21)	2.028(4)	Au(2)–S(6)–C(15)	113.7(1)
		Au(1)–C(1)–C(2)	121.3(3)
		Au(1)–C(1)–C(6)	124.1(3)

The ligand Et_4todit also reacts with [Au(tht)$_2$]OTf (OTf = triflate, CF_3SO_3) to give the dinuclear [Au(Et_4todit)]$_2$(OTf)$_2$ (**2**) (Scheme 1) as a yellow solid. It is soluble in dichloromethane and acetone and insoluble in diethyl ether and hexane. It has been characterized by [1]H-NMR spectroscopy and mass spectrometry. Single crystals suitable for X-ray diffraction analysis were obtained by slow diffsion of hexane in a solution of **2** in 1,2-dichloroethane, and the molecular structure is depicted in Figure 2. The two five-membered rings of the bis(thiocarbonyl) donors are twisted about the C–C bond by 72.65°. The two gold centers present a distorted linear geometry and are bonded to two C=S groups of the thioimidazole of different Et_4todit ligands. The S(1)–Au(1)–S(2) angle (174.8(1)°) and the Au(1)–S(1) (2.289(1) Å) and Au(1)–S(2) (2.294(1) Å) bond distances found in the solid structure are in good agreement with those reported in the literature [4,5]. No Au(I)–Au(I) intra- or inter-molecular interactions have been observed in the crystal structure. The complex is not luminescent in solid state or in solution.

Figure 2. Molecular structure of the compound **2**, with the atom labeling scheme (hydrogen atoms omitted for clarity).



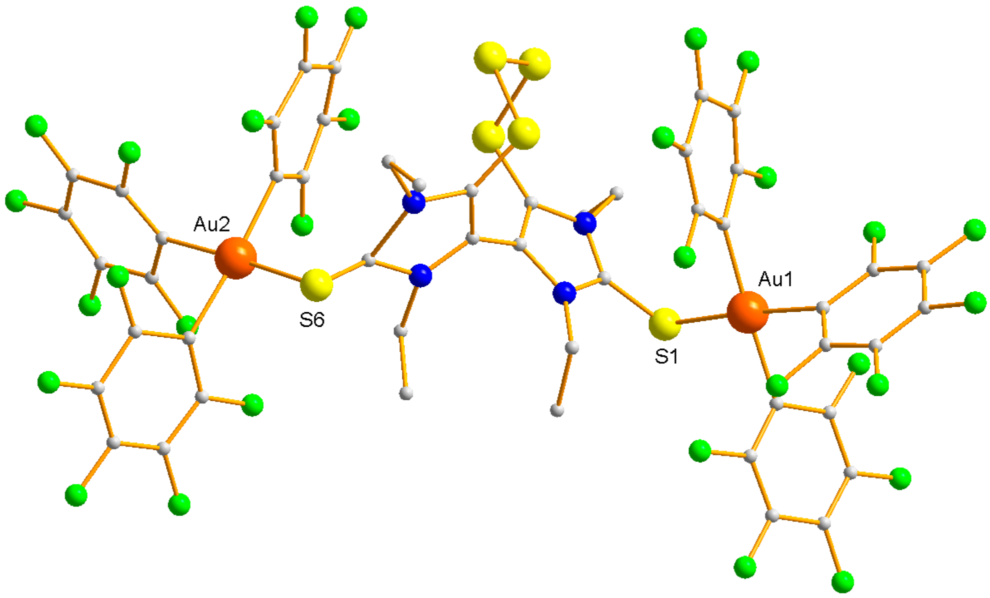
A selection of bond lengths and angles for complex **2** are summarized in Table 2.

Table 2. Selected bond lengths (Å) and angles (°) for **2**.

Distances (Å)		Angles (°)	
Au(1)–S(1)	2.289(1)	S(1)–Au(1)–S(2)	174.8(1)
S(2)–C(10)	1.729(3)	Au(1)–S(1)–C(1)	111.5(1)
S(2)–Au(1)	2.294(1)		
S(1)–C(1)	1.709(2)		

With the gold(III) complex $[Au(C_6F_5)_3(tht)]$ (molar ratio = 1:2) the dinuclear derivative $[\{Au(C_6F_5)_3\}_2(Et_4todit)]$ (**3**) was obtained (Scheme 1). The yellow solid is soluble in dichloromethane, acetone or diethyl ether, but insoluble in hexane. Complex **3** has been characterized by [1]H-NMR and [19]F-NMR spectroscopy and mass spectrometry. Single crystals were obtained by slow diffusion of hexane in a solution of complex **3** in 1,2-dichloroethane. Crystal structure has been elucidated and the proposed stoichiometry was confirmed, although (crystal system, triclinic; space group, P-1; cell: a, 12.6131; b, 13.2567; c, 18.3299 Å; α, 78.727; β, 74.371; γ, 82.645°; V, 2885.41; Z, 2) the quality of the data was not good. Thus, no comparison of bond distances and angles with other complexes can be made, although a molecular diagram is shown in Figure 3. The two gold centers present a distorted square-planar geometry and each one is bonded to the C=S groups of the thioimidazol rings and to three pentafluorophenyl groups.

Figure 3. Molecular structure of the compound **3** (hydrogen atoms omitted for clarity).



3. Experimental Section

3.1. Instrumentation

Mass spectra were recorded on a BRUKER (Bremen, Germany) ESQUIRE 3000 PLUS, with the electrospray (ESI) technique and on a BRUKER (Bremen, Germany) MICROFLEX (MALDI-TOF), with a Dithranol or a T-2-(3-(4-tbutyl-phenyl)-2-methyl-2-propenylidene)malononitrile matrix. Room-temperature NMR spectra were recorded with a Bruker (Karlsruhe,, Germany) ARX 400 spectrometer (^{1}H, 400 MHz and ^{19}F, 376.5 MHz). The chemical shifts are reported in ppm relative to the residual solvent peak [^{1}H $(CD_3)_2CO$: 2.05] and $CFCl_3$, respectively.

3.2. Starting Materials

Et_4todit [13,14], [Au(C_6F_5)(tht)] [15], [Au(tht)$_2$]OTf [16,17] and [Au(C_6F_5)$_3$(tht)] [15], were prepared according to literature procedures. Other starting materials and solvents were purchased from commercial suppliers and used as received unless otherwise stated.

*3.3. General Procedure for the Synthesis of the Complexes **1–3***

Synthesis of [{Au(C_6F_5)}$_2$(Et_4todit)] (**1**). A solution of [Au(C_6F_5)(tht)] (83.7 mg, 0.18 mmol) in dichloromethane (5 mL) was added to a solution of Et_4todit (40.4 mg, 0.09 mmol) in dichloromethane (5 mL). The mixture was stirred for two hours at room temperature and the solution was filtered through Celite. The complex **1** was obtained as white crystals by slow diffusion of hexane in the reaction mixture (92.8 mg, yield, 86.7%). ^{1}H-NMR (CD_3COCD_3, 400 MHz): δ 1.33 (6H, t, CH_3, *J*(HH) 7.1 Hz), 1.59 (6H, t, CH_3, *J*(HH) 7.1 Hz), 4.21 (2H, m, CH_2), 4.82 (4H, dt, CH_2, *J*(HH) 14.0 and 7.1 Hz), 4.98 (2H, m, CH_2). ^{19}F-NMR (CD_3COCD_3, 377 MHz): δ −165.6 (4F, m, *m*-F), −163.3 (2F, t, *p*-F, *J*(FF) 19.8 Hz), −117.8 (4F, m, *o*-F). MS (MALDI$^+$): *m*/*z* 1163.3 $[(M)^+$ 0.8%, *calculated:* 1163.9], 1101.4 $[(M - 2S + 2H)^+$ 4.0%], 933.3 $[(M - 2S - C_6F_5)^+$ 36.8%], 569.2 $[(M - 2S - C_{12}F_{10}Au)^+$ 100%]. Analytical data: $C_{26}H_{20}Au_2F_{10}N_4S_6$ (1163.92) requires C, 26.81; H, 1.73; N, 4.81; S, 16.52; found C, 26.72; H, 1.71; N, 4.66; S, 16.22.

Synthesis of $[Au(Et_4todit)]_2(OTf)_2$ (**2**). [Ag(tht)(OTf)] (51.2 mg, 0.15 mmol) was added to a solution of [AuCl(tht)] (47.6 mg, 0.15 mmol) in dichloromethane (25 mL). The mixture was stirred for three hours at room temperature and the AgCl precipitated was filtered off through Celite. To the filtered mixture a solution of Et_4todit (58.4 mg, 0.13 mmol) in dichloromethane (10 mL) was added dropwise and stirred for one hour at room temperature. The slightly yellow solution was concentrated under reduced pressure and solid was precipitated with hexane. The product was collected by filtration and recrystallized from dichloromethane/hexane (78.7 mg, yield: 75%). ^{1}H-NMR (400 MHz, CD_3COCD_3) δ 4.56 (4H, m, CH_2), 3.91 (4H, m, CH_2), 1.45 (6H, t, CH_3, *J*(HH) 7.1 Hz), 1.19 (6H, t, CH_3, *J*(HH) 7.1 Hz). MS (MALDI$^+$): *m*/*z* 1414.9 $[(M - CF_3SO_3)^+$ 4%] *calculated*: 1414.89, 1266 $[(M - 2CF_3SO_3)^+$ 10%], *calculated*: 1265.94. Analytical data: $C_{30}H_{40}Au_2F_6N_8O_6S_{14}$ (1563.84) requires C, 23.02; H, 2.58; N, 7.16; S, 28.67; found C, 23.14; H, 2.44; N, 7.01; S, 28.17.

Synthesis of $[\{Au(C_6F_5)_3\}_2(Et_4todit)]$ (**3**). $[Au(C_6F_5)_3(tht)]$ (95.4 mg, 0.12 mmol) was added to a solution of Et_4todit (26.5 mg, 0.06 mmol) in dichloromethane (8 mL) and the mixture was stirred for two hours at room temperature. The slightly yellow solution was concentrated under reduced pressure and solid was precipitated with hexane. The yellow product was collected by filtration and recrystallized from dichloromethane/hexane (51.0 mg, yield: 46%). ^{1}H-NMR (400 MHz, CD_3COCD_3) δ 4.90 (2H, m, CH_2), 4.59 (4H, m, CH_2), 4.26 (2H, m, CH_2), 1.44 (12H, m, CH_3). ^{19}F-NMR (377 MHz, CD_3COCD_3) δ −122.42 (4F, m, *o*-F), −122.57 (4F, m, *o*-F), −124.17 (4F, m, *o*-F), −159.42 (4F, t, *J*(FF) 19.7 Hz), −160.53 (2F, t, *J*(FF) 19.5 Hz), −163.04 (4F, m, *m*-F), −164.67 (8F, m, *m*-F). MS (MALDI$^+$): *m*/*z* 1263.3 $[(M - 3C_6F_5 - 2S)^+$ 10.1%] *calculated*: 1267.0, 1101.2 $[(M - 4C_6F_5 - 2S)^+$ 8.7%], 933.3 $[(M - 2S - 5C_6F_5)^+$ 11.1%], 736.2 $[(M - 3S - 6C_6F_5 + 2H)^+$ 26.3%]. Analytical data: $C_{50}H_{20}Au_2F_{30}N_4S_6$ (1831.89) requires C, 32.76; H, 1.10; N, 3.06; S, 10.50; found C, 32.34; H, 1.44; N, 3.01; S, 10.17.

3.4. Cristallography

Crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of Xcalibur (Agilent Technologies, Waldbronn, Germany) Oxford Diffraction (**3**) diffractometer equipped with a low-temperature attachment. Data were collected using monochromated Mo Kα radiation (λ = 0.71073 Å). Scan type ω. Absorption correction based on multiple scans were applied using spherical harmonics implemented in SCALE3 ABSPACK [18] scaling algorithm. The structures were solved by direct methods and refined on F^2 using the program SHELXL-97 [19], All non-hydrogen atoms were refined anisotropically. Refinements were carried out by full-matrix least-squares on F^2 for all data. Further details of the data collection and refinement are given in Table 3. CCDC-1006288 (**1**) and 1006289 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre [20].

Table 3. Details of Data Collection and Structure Refinement for Complexes **1** and **2**.

Compound	1	$2·2CH_2Cl_2$
Chemical Formula	$C_{26}H_{20}Au_2F_{10}N_4S_{12}$	$C_{32}H_{44}Au_2Cl_4F_6N_8O_6S_{14}$
Appearance	Colorless plate	Colorless needle
Crystal size/mm	0.42 × 0.23 × 0.06	0.20 × 0.08 × 0.06
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a/Å	9.97740(10)	9.7616(2)
b/Å	12.1758(2)	12.9096(3)
c/Å	14.0916(2)	13.0537(3)
α/°	73.7730(10)	63.202(2)
β/°	82.3940(10)	77.979(2)
γ/°	88.3680(10)	76.346(2)
U/Å^3	1629.16(4)	1416.97(5)
Z	2	1
D_C/g cm^{-3}	2.374	2.034
M	1164.75	1735.33
F(000)	1096	844
T/°C	−173	−173
$2θ_{max}$/°	51	51
μ(Mo-Kα)/mm^{-1}	9.465	5.943
Transmission	0.6005, 0.1092	0.7169, 0.3828
No. of reflections measured	29873	27048
No. of unique reflections	6032	5254
R_{int}	0.038	0.018
R^a ($F > 4σ(F)$)	0.024	0.045
$wR2$ (F^2, all refl.)	0.066	0.175
No. of reflections used	6032	5254
No. of parameters	437	329
S	1.059	1.041
Max. Δρ/eÅ^{-3}	1.77	0.90

4. Conclusions

The reaction of the ligand Et_4todit with some gold(I) or gold(III) complexes leads to the dinuclear [{Au(C_6F_5)}$_2$(Et_4todit)] (**1**), [Au(Et_4todit)]$_2$(OTf)$_2$ (**2**) or [{Au(C_6F_5)$_3$}$_2$(Et_4todit)] (**3**). They represent some of the few examples of thione gold derivatives, and because the stability of the complexes the bond Au-S within these complexes may be strong. They do not contain intra- or inter-molecular gold-gold interactions, probably because steric effects of the ligand, and they are not luminescent in solid state or in solution.

Acknowledgments

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Author Contributions

The synthesis and spectroscopic characterization of the new complexes were performed by Francesco Caddeo and Vanesa Fernández-Moreira. The synthesis of the ligand was carried out by Vito Lippolis and Massimiliano Arca. The X-ray structures were carried out by M. Concepción Gimeno. The expertise in gold chemistry and methodology was provided by M. Concepción Gimeno and Antonio Laguna. Data analysis and preparation of the manuscript were made by all the authors.

Conflicts of Interest

The authors declare no conflict of interest.

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