

## Synthesis of the First Trithiocarbonatogold complex: $[N(PPh_3)_2]_2[Au_2(\mu^2-\eta^2-CS_3)_2]$ . First Crystal Structure of a $\mu^2-\eta^2$ -Bridging Trithiocarbonato Complex

José Vicente,<sup>\*a</sup> María-Teresa Chicote,<sup>\*a</sup> Pablo González-Herrero<sup>a</sup> and Peter G. Jones<sup>\*b</sup>

<sup>a</sup> Grupo de Química Organometálica, Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia, Apto. 4021, E-30071 Murcia, Spain (E-Mail, JVS@FCU.UM.ES)

<sup>b</sup> Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany

The reaction of  $[N(PPh_3)_2][Au(SH)_2]$  with  $CS_2$  gives  $[N(PPh_3)_2]_2[Au_2(\mu^2-\eta^2-CS_3)_2]$  whose crystal structure shows planar  $[Au_2(\mu^2-\eta^2-CS_3)_2]^{2-}$  anions and two  $[N(PPh_3)_2]$  cations; the coordination at gold is almost linear  $[SAuS 172.80(5)^\circ]$  and both gold atoms are doubly bridged by  $CS_3$  anions, associated with a very short  $Au\cdots Au$  contact of 2.7998(4) Å.

Sulfur-donor ligands can connect metal centres in di- or polynuclear complexes and are useful as catalysts or solid state materials; they are also present in biological systems.<sup>1</sup> Interest in complexes containing Au–S bonds stems from the potential application in medicine (chrysotherapy),<sup>2</sup> and in the glass and ceramic industries.<sup>3</sup> Thus, thiolatogold(I) complexes, such as the commercial antiarthritic Myocrisin, Allochrysin, Solganol or Auranofin, are among the most important antiarthritic compounds.<sup>2</sup> In addition, Solganol has *in vitro* inhibitory effects on Human Immunodeficiency Virus 1, which is the etiologic agent of AIDS,<sup>4</sup> and Auranofin was found to be highly cytotoxic to tumour cells<sup>5</sup> and active against i.p. P388 leukaemia.<sup>6</sup>

Trithiocarbonates have received attention due to their activity as antiwear and antioxidant additives to extreme pressure lubricant oils and greases.<sup>7</sup> Interest in trithiocarbonato complexes stems from the dual nature of the metal– $CS_3$  moiety as an electrophilic and nucleophilic reagent, which makes them versatile intermediates for the synthesis of other thio species.<sup>8</sup> However, few trithiocarbonato metal complexes have been synthesized and fully characterized.<sup>9–17</sup> Thus, as far as we are aware only a few complexes (of V,<sup>10</sup> Fe,<sup>11</sup> Mo,<sup>12</sup> Re,<sup>13</sup> Co,<sup>14</sup> Ni,<sup>15</sup> Pd,<sup>16</sup> Pt,<sup>16</sup> and Cu<sup>17</sup>) have been studied by X-ray diffraction and only one is a homoleptic complex:  $[Ni(CS_3)_2]^{2-}$ .<sup>15a</sup> Most of the other reported complexes are poorly characterized because, even in the best cases, only elemental analyses (generally excluding sulfur), IR and NMR (always excluding <sup>13</sup>C NMR to prove the presence of the  $CS_3^{2-}$  ligand) have been reported.<sup>8,18</sup> Trithiocarbonato usually coordinates as chelating ligand (see A Fig. 1) although the  $[M]S_2CS$  moiety can act as a ligand to bind one **B** or two metal centres **C**.<sup>8–18</sup> In one case only it has been reported to behave as a  $\mu^4-\eta^8$ -bridging ligand **D**.<sup>17</sup> In this paper we report the first crystal structure of a trithiocarbonato complex acting as a  $\mu^2-\eta^2$ -bridging ligand **E**.

The general synthetic methods for trithiocarbonato complexes include reaction of  $CS_2$  with oxo-,<sup>18a</sup> sulfido-,<sup>10,12</sup> dithiocarbonato-,<sup>18ef</sup> carbonyl- or carbonylato-complexes,<sup>13,14,18c</sup> and reaction of trithiocarbonato salts with aquo-,<sup>8a,d</sup> acetato-,<sup>18g</sup> halo-,<sup>14,17,18h</sup> or perchlorato-complexes.<sup>18i</sup>

We report here the reaction of  $[N(PPh_3)_2][Au(SH)_2]$ <sup>20</sup> with  $CS_2$  to give  $[N(PPh_3)_2]_2[Au_2(\mu^2-\eta^2-CS_3)_2]$  [eqn. (1)] **1**† which

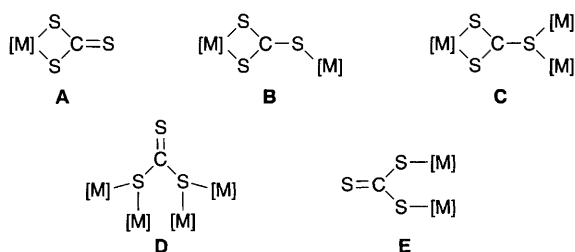
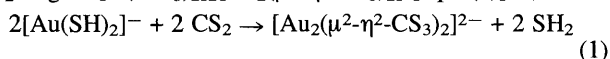
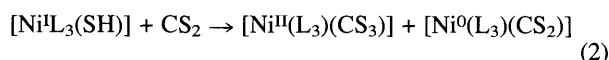


Fig. 1

is the first trithiocarbonato gold complex and one of the few homoleptic trithiocarbonato complexes of any element. Although the sodium or potassium trithiocarbonato salts can be obtained by treating the corresponding hydrosulfides with  $CS_2$ ,<sup>20</sup> we only know one precedent for our method of synthesis. However, it involves a disproportionation reaction, eqn. (2).<sup>8b</sup> The reaction of the hydrogensulfido complex



$[Ir(C_5Me_5)(H)(SH)(PMe_3)]$  with  $CS_2$  has been reported to give a dithioformate complex due to  $CS_2$  insertion into the metal–hydrogen bond rather than into the metal–sulfur bond.<sup>21</sup> We have unsuccessfully attempted to prepare **1** more directly by reacting  $[N(PPh_3)_2][AuCl_2]$  with  $K_2CS_3$ .

The solid state IR spectrum of **1** shows, apart from bands due to the cation, strong bands at 940, 927 and 910  $cm^{-1}$  assignable to  $\nu(CS)$  modes. Other trithiocarbonato complexes show bands corresponding to the  $\nu(C=S)$  and  $\nu(C-S)$  modes in the 990–1054 and 850–885  $cm^{-1}$  ranges, respectively.<sup>8–18,22</sup> The IR spectrum of the starting material  $[N(PPh_3)_2][Au(SH)_2]$  shows a band at 340  $cm^{-1}$  that we have assigned to  $\nu(AuS)$ .<sup>19</sup> In trithiocarbonato complexes a band in the same region has been assigned to the  $\nu(MS)$  mode ( $M = Ni, Pd, Pt$ ).<sup>22</sup> Although in **1** there are several bands around 340  $cm^{-1}$ , they are too weak to be assigned. As far as we are aware, only two papers report <sup>13</sup>C NMR spectra of trithiocarbonato complexes.<sup>10,12a</sup> The <sup>13</sup>C NMR resonance associated with the  $CS_3^{2-}$  group in **1** ( $\delta$  251.6) is near the range  $\delta$  253–255 reported for other complexes.

The crystal structure of **1** (Fig. 2) shows a planar (centrosymmetric)  $[Au_2(\mu^2-\eta^2-CS_3)_2]$  dianion (mean deviation from the best plane 0.03 Å) and two  $[N(PPh_3)_2]$  cations.† The coordination at gold is almost linear  $[SAuS 172.80(5)^\circ]$  and both gold atoms are doubly bridged by  $CS_3$  moieties, with a very short  $Au\cdots Au$  contact of 2.7998(4) Å (the Au–Au distance in the metal is 2.884 Å<sup>23a</sup>). Only a few complexes with similar or shorter  $Au\cdots Au$  contacts have been reported.<sup>23</sup> The AuS bond distances [2.304(2), 2.293(2) Å] are similar to those found in

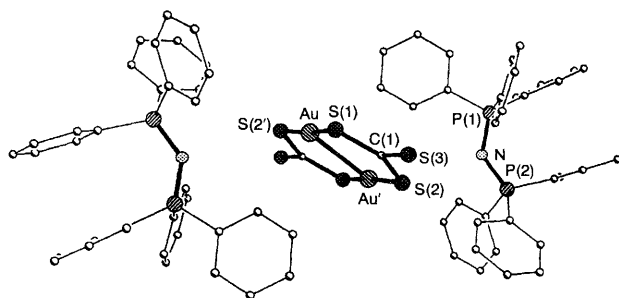


Fig. 2 The structure of complex **1** in the crystal (H atoms omitted; radii are arbitrary). Selected bond distances (Å) and angles ( $^\circ$ ): Au–S(1) 2.304(2), Au'–S(2) 2.293(2), Au–Au' 2.7998(4), C(1)–S(1) 1.726(6), C(1)–S(2) 1.742(6), C(1)–S(3) 1.672(6), S(2')–Au–S(1) 172.80(5), S(3)–C(1)–S(1) 118.4(4), S(3)–C(1)–S(2) 115.7(3), S(1)–C(1)–S(2) 125.9(3), P(1)–N–P(2) 135.4(3).

some thiolatogold(I) complexes.<sup>24</sup> The CS<sub>3</sub><sup>2-</sup> bond lengths and angles are similar to those found in the bridging CS<sub>3</sub><sup>2-</sup> groups of the complex [Cu<sub>4</sub>(μ<sup>4</sup>-η<sup>8</sup>-CS<sub>3</sub>)<sub>2</sub>{bis(diphenylphosphino)methane}] (see **D** Fig. 1).<sup>17</sup> The main difference is that the S(1)–C(1)–S(2) bond angle is greater in **1** [125.9(3)°] than the corresponding angle in the copper complex [122(1)°].

In an attempt to prepare [(AuPPh<sub>3</sub>)<sub>2</sub>(μ-S<sub>2</sub>CS)] we treated [AuCl(PPh<sub>3</sub>)] with K<sub>2</sub>CS<sub>3</sub> in 2 : 1 molar ratio but [S(AuPPh<sub>3</sub>)<sub>2</sub>], KCl and CS<sub>2</sub> were formed instead. At present we are exploring different ways of preparing gold(I), (II) and (III) trithiocarbonato complexes and are studying the reactivity of complex **1**.

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### Footnotes

† A solution of [N(PPh<sub>3</sub>)<sub>2</sub>][Au(SH)<sub>2</sub>] (120.5 mg, 0.15 mmol) in a mixture of CS<sub>2</sub> (6 ml)–acetone (2 ml) was stirred at room temp. for 20 h. The orange–yellow precipitate formed was filtered off, washed with acetone (3 ml) and diethyl ether (5 ml) and air dried to give **1** (110.5 mg, 0.13 mmol, 87%). Mp 202 °C. IR ν/cm<sup>-1</sup> 940, 927, 910. <sup>13</sup>C NMR [(CD<sub>3</sub>)<sub>2</sub>SO, SiMe<sub>4</sub>] δ 251.6 (CS<sub>3</sub>).

‡ Crystal data for **1**: C<sub>74</sub>H<sub>60</sub>Au<sub>2</sub>N<sub>2</sub>P<sub>4</sub>S<sub>6</sub>, M<sub>r</sub> = 1687.4, triclinic, P $\bar{1}$ , T = 173 K, a = 11.0473(10), b = 11.6088(10), c = 14.2666(14) Å, α = 109.572(6), β = 106.693(6), γ = 93.019(6)°, V = 1628.6(3) Å<sup>3</sup>, Z = 1, λ (Mo-Kα) = 0.71073 Å, μ = 4.8 mm<sup>-1</sup>, D<sub>c</sub> = 1.720 Mg m<sup>-3</sup>. Data collection: Colourless prism 0.6 × 0.5 × 0.15 mm, Siemens P4 diffractometer, 5343 unique intensities, 2θ<sub>max</sub> 50°, absorption correction with SHELXA (G. M. Sheldrick, unpublished) with transmissions 0.236–0.707. Structure solution and refinement: Heavy-atom method, refined anisotropically on F<sup>2</sup> (program SHELXL-93, G. M. Sheldrick, University of Göttingen), H atoms with riding model, wR(F<sup>2</sup>) 0.104, R(F) 0.040, 397 parameters, 389 restraints (to light atom displacement parameters and local ring symmetry), S = 1.01, max. Δρ 2.09 e Å<sup>-3</sup>. Full details of the structure have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. Any request for this material should quote a full literature citation and the reference number CSD 401511. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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