

Unusual Resonance Structures of Organic Thiones formed and stabilized by Gold(I) Complexation. The Isolation and Characterization of an Alkyl Substituted Thiabenzenthione and a Trithiapentalene Co-ordinated to Gold(I)

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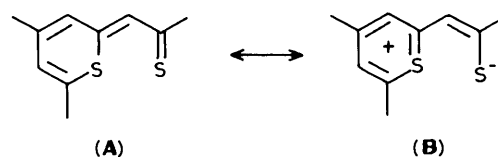
An alkyl substituted thiabenzenthione molecule and a trithiapentalene molecule displaying an unusual resonance form have been isolated by co-ordination to an Au^I centre; their structures have been determined by single-crystal X-ray diffraction analyses.

The interactions of Au^I complexes with sulphur-containing organic substrates are of interest owing to their important roles in industrial, environmental, and biological systems.¹ We have now found that Au^I complexes are able to stabilize certain unusual organosulphur species by the formation of Au-S bonds.

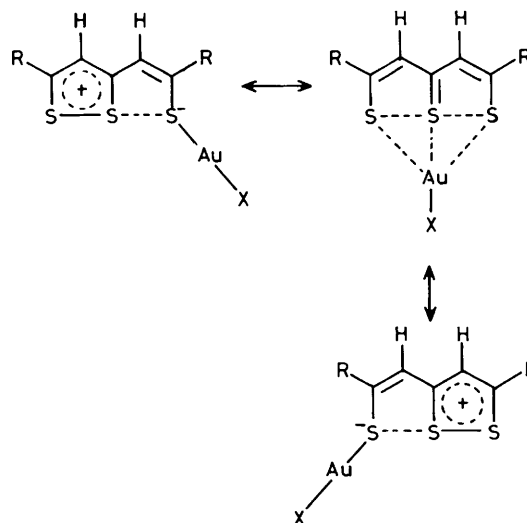
The reaction of 3,5-dimethyl-1,2-dithiolium bromide² (**1b**) (Scheme 1), with Au(tht)Cl (tht = tetrahydrothiophene) in CH₂Cl₂ at 23 °C, produced a purple compound (**3**) (33% yield) which was characterized by ¹H n.m.r. spectroscopy[†] and X-ray diffraction analysis.[‡]

The molecular structure and important bond distances and angles for (**3**) are given in Figure 1. This molecule consists of a methyl substituted thiabenzenthione ligand (**2c**), bonded to the Au^IBr through one of the sulphur atoms. The S-Au-Br angle of 178.3(1)^o is typical for two-co-ordinated Au^I complexes. The three S-C bonds range from 1.72(1) to 1.75(2) Å, indicating significant π-bonding. The C-C bond distances on the six-membered ring are in the range 1.35(2)—1.42(3) Å. Therefore, this ring can be best described as a thiabenzene cation. The S(1) ··· S(2) distance, 2.98 Å, is much longer

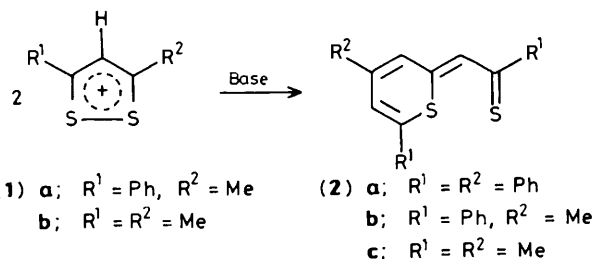
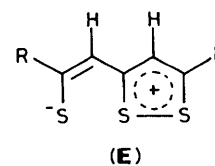
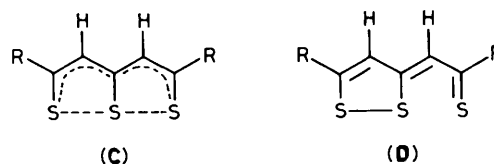
than an S-S single bond, but considerably shorter than twice the van der Waals radius³ for a sulphur atom (1.76 Å). The bonding distance between C(2) and C(3), 1.36(3) Å, is much shorter than that of C(3)-C(4), 1.48(3) Å. Apparently the zwitterion (or ylide) resonance form **B** is stabilized by co-ordination to the Au^I centre (see Scheme 2).



Scheme 2



Scheme 3



Scheme 1

[†] ¹H N.m.r. data for (**3**): (CD₂Cl₂), δ 2.45 (s, Me), 2.70 (s, Me), 7.11 (s, CH), 7.30 (s, CH), 7.41 (s, CH). For (**4a**): (CDCl₃) 7.45—7.59 (m, Ph), 7.81—7.92 (m, pH), 8.06 (s, 2H). For (**4b**) (CDCl₃) δ 7.20—7.60 (m, Ph), 7.90—8.00 (m, Ph), 8.65 (s, 2H). For (**4c**): (CDCl₃) δ 7.18—7.60 (m, Ph), 7.95—8.05 (m, Ph), 8.57 (s, 2H).

[‡] Crystal data for (**3**): C₁₀H₁₂AuBrS₂, *M* = 472.9, monoclinic, space group, *P*2₁/*a*, *a* = 8.767(2), *b* = 11.641(3), *c* = 13.088(4) Å, β = 107.95(2)^o, *U* = 1270.7(6) Å³, *Z* = 4, *D_c* = 2.47 g cm⁻³. For (**4a**): C₁₇H₁₂S₃AuCl·CH₂Cl₂, triclinic, *P*1̄, *a* = 9.066(3), *b* = 9.138(7), *c* = 12.913(5) Å, α = 84.93(5), β = 73.02(3), γ = 80.33(5)^o, *U* = 1007(1) Å³, *Z* = 2, *D_c* = 2.07 g cm⁻³. Data were collected on a Nicolet R 3m/E diffractometer. Structure solution and refinements were carried out using SHELXTL. The structures were solved by direct methods. Convergence to final *R* values of *R* = 0.0495 and *R_w* = 0.0528 for (**3**) was obtained by using 1149 reflections [*F*² ≥ 3σ(*F*²)]. Convergence to final *R* values of *R* = 0.0312 and *R_w* = 0.0308 for (**4a**) was obtained by using 1762 reflections [*F*² > 3σ(*F*²)]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

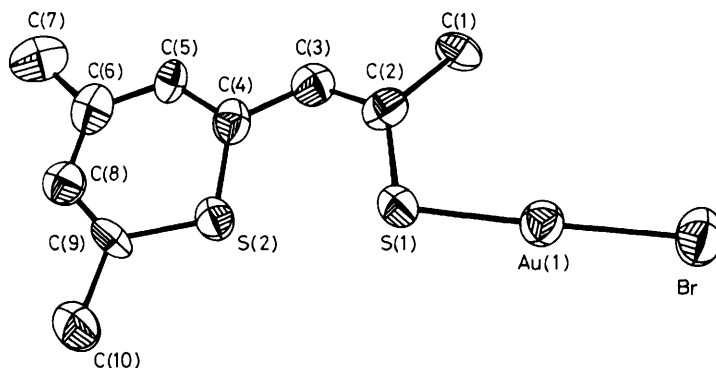


Figure 1. Structure of $(C_{10}H_{12}S_2)AuBr$ (**3**). Bond lengths: Au(1)–Br 2.393(3), Au(1)–S(1) 2.262(6), S(1)–C(2) 1.75(2), S(2)–C(4) 1.72(2), S(2)–C(9) 1.73(2), C(2)–C(3) 1.36(3), C(3)–C(4) 1.48(3), C(4)–C(5) 1.40(3), C(5)–C(6) 1.42(3), C(6)–C(8) 1.41(3), C(8)–C(9) 1.35(3) Å.

Bond angles: S(1)–Au(1)–Br 178.3(1), Au(1)–S(1)–C(2) 106.2(7), S(1)–C(2)–C(3) 121(2), C(2)–C(3)–C(4) 132(2), C(3)–C(4)–C(5) 119(2), C(4)–C(5)–C(6) 125(2), C(5)–C(6)–C(8) 121(2), C(6)–C(8)–C(9) 125(2), C(8)–C(9)–S(2) 124(2), C(9)–S(2)–C(4) 104(1), S(2)–C(4)–C(3) 120(2)°.

Although self-condensation reactions of dithiolium salts [Scheme 1. (**1a**; $R^1 = Me$, $R^2 = Ph$)] have been described previously by Leaver *et al.*,⁴ reactions for 3,5-dialkyl-1,2-dithiolium salts ($R^1 = R^2 = alkyl$) remain unknown. Compounds (**2a**) and (**2b**) can be prepared by a few synthetic routes.^{4,5} However, their analogue (**2c**) has not been synthesized, apparently owing to the poor stability of alkyl substituted thiones.⁶ In the absence of the Au^I , (**2c**) undergoes further condensation. Leaver *et al.* have proposed that such dithiolium self-condensation reactions are base-catalysed.^{4b}

Although the mechanism of the Au^I -catalysed reaction is not clear, it is reasonable to assume that the Au^I functions as a stabilizing agent for (**2c**) and also as a base to cause the dithiolium condensation. The isoelectronic species, $Pt(PR_3)_2$, is known to function as a base in selected catalytic reactions.⁷ Efforts to release (**2c**) from the Au^I complex by complexation of the Au^I with pyridine failed, presumably due to the instability of (**2c**) in the medium.

The facile formation of a trithiapentalene Au^I complex further demonstrates the ability of Au^I complexes to stabilize unusual sulphur-containing species. Reactions of 2,5-diphenyl-1,6,6a-trithiapentalene⁸ with $Au(tht)Cl$ or $Au(PPh_3)NO_3$ at 23°C result in the formation of dark red compounds $Au(tp)Cl$ (**4a**) (30% approx. yield), and $Au(tp)(PPh_3)NO_3$ (**4b**) ($tp =$ trithiapentalene), respectively. $Au(tp)(PPh_3)BF_4$ (**4c**) was isolated in crystalline form by the addition of $Bu^n_4NBF_4$ to the solution of (**4b**) (82% yield). These new compounds were characterized by 1H n.m.r. spectroscopy,[†] elemental analyses,[‡] and single-crystal X-ray diffraction.[‡]

The molecular structure of (**4a**) and some important bond lengths and angles are shown in Figure 2. This compound contains a co-ordinated tp ligand that is *unsymmetrical*. The S(1)–S(2) distance is 2.745(4) Å, while the S(2)–S(3) distance is 2.096(4) Å, typical for a S–S single bond. The three sulphur atoms are co-linear, S(1)–S(2)–S(3) 176.4°. The five-membered ring S(2)–S(3)–C(5)–C(4)–C(3) can be described as a typical dithiolium cation. The zwitterion resonance form (**E**), is stabilized by complexation to the Au^I centre.

Previous studies^{6,8} with X-ray diffraction, n.m.r., u.v., and ESCA, *etc.*, on the structures of symmetrically substituted trithiapentalene molecules have revealed that these molecules

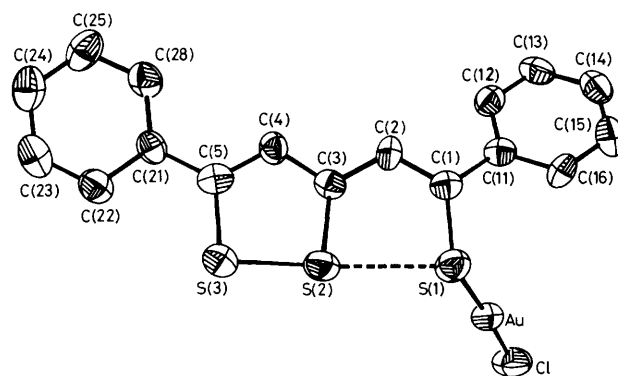


Figure 2. Structure of the $(tp)AuCl$, (**4a**). Bond lengths: Au–S(1) 2.258(2), Au–Cl 2.277(3), S(1)···S(2) 2.745(4), S(2)–S(3) 2.096(4), S(1)–C(2) 1.75(1), S(2)–C(3) 1.72(1), S(3)–C(5) 1.70(1), C(1)–C(2) 1.39(1), C(2)–C(3) 1.44(1), C(3)–C(4) 1.41(1), C(4)–C(5) 1.39(1), C(1)–C(11) 1.49(1), C(5)–C(21) 1.47(1) Å.

Bond angles: S(1)–Au–Cl 176.1(1), Au–S(1)–C(1) 106.0(3), S(1)–C(1)–C(2) 118.3(7), S(1)–C(1)–C(11) 121.5(7), C(1)–C(2)–C(3)–125(1), C(2)–C(3)–C(4) 119.0(9), C(3)–C(4)–C(5) 118.2(9), C(4)–C(5)–C(21) 125.3(9), C(4)–C(5)–S(3) 115.4(8), C(5)–S(3)–S(2) 96.4(3), S(3)–S(2)–C(3) 93.9(3), S(2)–C(3)–C(4) 116.2(6)°.

tend to exist in the resonance form (**C**), both in solutions and solid state. In fact, no valence isomers such as (**D**) or (**E**) have been found, perhaps because of their relative instability.^{8‡‡} It is believed that (**4b**) and (**4c**) are structures analogous to (**4a**).

These compounds are the first examples of symmetrically substituted trithiapentalene molecules isolated in non-symmetrical resonance forms. Obviously the Au^I sulphur bonding plays an important role in stabilizing these unusual valence structures.

Compounds (**4a–c**) are fluxional in solution. Only one vinylic proton signal (singlet) is observed in their 1H n.m.r. spectra[†] at 22°C. The coalescence temperature^{††} of $-110 \pm 2^\circ C$ was observed in variable temperature 1H n.m.r. spectra for (**4c**). The fluxionality of these molecules can be described

‡‡ Unequal S–S bond lengths have been observed in a few unsymmetrically substituted or sterically crowded tp molecules.⁸

†† Owing to the limit of the solvent, the slow exchange proton signals have not been observed. Assuming that the chemical shifts for the protons in (**E**) can be taken from shifts for similar known compounds^{2,13}, a E_a of ~ 7 – 8 kcal/mol (cal = 4.184 J) is estimated for the exchange process.

§ This compound was synthesized by the reaction of $PhCS_2H$ with 3-methyl-5-phenyl-1,2-dithiolium iodide.

¶ Satisfactory elemental analyses were obtained for (**4a**) and (**4c**).

by an intramolecular exchange process such as shown in Scheme 3.

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