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Complexes with S-Donor Ligands. 6.[†] Synthesis of the First Family of (Trithiocarbonato)gold Complexes. Crystal Structure of $[(PPh_3)_2N][AuCl_2(CS_3)]$

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$[(PPh_3)_2N][Au(SH)_2]$ reacts with CS_2 in acetone to give $[(PPh_3)_2N]_2[Au_2(CS_3)_2]$ (**1**) which reacts with iodine (1:1) or $PhICl_2$ (1:1) to give **2** or **2′**, which is an equimolar mixture of the gold(III) complex $[(PPh_3)_2N][Au(CS_3)_2]$ (**3**) and $[(PPh_3)_2N][AuX_2]$ (X = I, Cl). These mixtures decompose in dichloromethane or acetone solutions giving an insoluble dark-red solid analyzing as the mixed-valence complex $[(PPh_3)_2N][Au^I_n\{Au^{III}(CS_3)_2\}_{n+1}]$ (**4**) with an average *n* value of 6. The best method to prepare **3** is by reacting **2** with PTo_3 (To = C_6H_4Me-4). The reaction of **4** with $[Et_2NC(S)S]_2$ gives $[Au(S_2CCNEt_2)_2][Au(CS_3)_2]$ (**5**), which can also be obtained by reacting **3** with $[Au(S_2CNEt_2)_2]ClO_4$. The complex $[(PPh_3)_2N][AuCl_2(CS_3)]$ (**6**) can be obtained by reacting **3** with $PhICl_2$ (1:1) or **1** with $PhICl_2$ (1:2). By reaction of **6** with an excess of NaBr, the complex $[(PPh_3)_2N][AuBr_2(CS_3)]$ (**7**) can be isolated. Iodine reacts with **3** (1:1) to give $[(PPh_3)_2N][AuI_2(CS_3)]$ (**8**). Cationic complexes $[Au(CS_3)(LL)]CF_3SO_3$ [LL = 1,10-phenanthroline (phen) (**9**), 2,2′-bipyridyl (bipy) (**10**)] can be obtained by reacting **6** with TlO_3SCF_3 and the corresponding bidentate ligand (1:2:1). Complex **6** crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 9.482(2)$ Å, $b = 11.888(2)$ Å, $c = 17.303(2)$ Å, $\alpha = 108.236(6)°$, $\beta = 93.340(10)°$, $\gamma = 95.605(10)°$, $V = 1835.5$ Å^3, and $Z = 2$. The structure was refined to values of R1 = 0.0393 [$I > 2\sigma(I)$] and wR2 = 0.0970 (all data). The planar coordination at the gold atom is distorted by the bite of the CS_3 ligand [the S(2)−Au−S(1) angle is only 74.49(7)°]. The CS_{Au} bond distances are 1.743(7) and 1.748(7) Å, whereas the CS_{exo} bond is much shorter at 1.608(7) Å.

Introduction

Gold(I) complexes with S-donor ligands are of interest because of their potential use in medicine (chrysotherapy).[1] Although the main application is the treatment of a variety of rheumatic diseases, some of these compounds have been shown to have antileishmanial activity,[1a] *in vitro* inhibitory effects on HIV 1,[2] or activity against tumor cells.[3]

Trithiocarbonates are used as antiwear and antioxidant additives to extreme pressure lubricant oils and greases.[4] Trithiocarbonate complexes have received attention because of 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 by their participation in (i) alkylation at the exocyclic sulfur atom, (ii) displacement of weakly bound ligands from metal complexes, (iii) reaction with unsaturated species to give binuclear complexes, (iv) cycloaddition of activated alkynes, (v) sulfur extraction to give CS_2 complexes, or (vi) sulfur addition to give CS_4^{2-} complexes.[5]

Despite their synthetic and practical utility, few (trithiocarbonato)metal complexes have been fully characterized including X-ray crystal structure (V,[6] Mo,[7] Re,[8] Fe,[9] Co,[10] Ni,[11] Pd, Pt,[12] Cu,[13] Zn, Sn, As, Sb, Bi[9c,14]). In most cases, the ligand acts as a chelate, but a small number of examples are known in which

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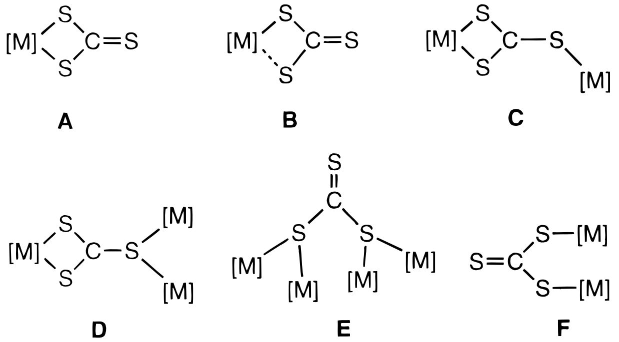
Chart 1



it coordinates as a unidentate ligand (or unsymmetrical chelate; see **B** in Chart 1)[9c,14] or as a μ_2-η^3- (see **C** in Chart 1),[12] μ_3-η^3- (see **D** in Chart 1),[8] or μ_4-η^2-ligand (see **E** in Chart 1).[13] We report here a gold(I) complex showing an μ_2-η^2-trithiocarbonato ligand (see **F** in Chart 1) and the first crystal structure of a (trithiocarbonato)gold(III) complex. These and the other CS_3 complexes (Ti,[14] V,[16] Cr,[5a,17] Mo,[18] Mn, Re,[5c] Fe,[16] Co,[5a,b,17,19] Rh,[20] Ni,[5a,b,16,19a,21] Pd,[21c,d,22] Pt,[21c,d,22d,23] Cu,[16,17,24] Ag,[16] Zn, Cd,[16,17] Tl,[16] Sn,[17] As, Sb, Bi,[17] and U[16,25]) have been prepared by reacting (i) CS_2 with oxo,[15] sulfide,[6,7a,26] dithiocarbonate,[20] carbonyl,[8,10] or carbonylate complexes;[5c] (ii) trithiocarbonato complexes or salts with aquo,[5a,19a,24] acetato,[16] perchlorato,[22a] halo,[10,21a,d] acetylacetonato,[9b,c,14] sulfide,[14,26] or thf complexes;[5a,12,19a] (iii) sulfur with CS_2[5b,c,14] or with NaOEt and R_3PCS_2 complexes;[19b] (iv) PPh_3 with perthiocarbonato[21b,26] or CS_2[33] complexes; or (v) by decomposition of a xanthato complex.[11c] We report here the synthesis of the first (trithiocarbonato)gold(I) complex by reacting $[Au(SH)_2]^-$ with CS_2. As far as we are aware, there is only one precedent for this method, which however involved a disproportionation reaction ($[Ni^{I}L_3(SH)] + CS_2 \rightarrow [Ni^{II}L_3(CS_3)] + [Ni^{0}L_3(CS_2)] + ...$).[5b] A related reaction is that of $[(MeCp)Mo(S)(SH)]_2$ with Cl_2CS giving $[(MeCp)_2Mo_2(CS_3)(C_2H_2S_2)]$.[18] We also report the first CS_3–gold(III) complexes using an unprecedented method: the halogen oxidation of a trithiocarbonato complex. Some of these results have been the subject of a preliminary communication.[27]

Experimental Section

Infrared spectra were recorded in the range 4000−200 cm^{-1} on a Perkin-Elmer 16F PC FT-IR espectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured with a Philips PW9501 conductimeter. Melting points were determined on a Reicher apparatus and are uncorrected. C, H, N, and S analyses were carried out with a Carlo Erba 1106 microanalyzer. ^{13}C NMR were measured on a Varian Unity 300 spectrometer. Mass spectra (FAB$^-$) were measured with a Fisons VG-Autospec spectrometer using 3-nitrobenzyl alcohol as matrix. All solvents were distilled before use, and unless otherwise stated, the reactions were carried out under normal laboratory conditions.

$[Au(S_2CNEt_2)_2]ClO_4$ was prepared by reacting equimolar amounts of $[Au(S_2CNEt_2)_2][AuCl_2]$[28] and $[(PPh_3)_2N]ClO_4$ in acetone (satisfactory elemental analyses, 84% yield). $PhICl_2$ was prepared by bubbling chlorine into PhI for 10 min, filtering the pale yellow solid formed, washing it with *n*-hexane, and drying in the air.

$[(PPh_3)_2N]_2[Au_2(CS_3)_2]$ (1). A solution of $[(Ph_3P)_2N][Au(SH)_2]$ (120.5 mg, 0.150 mmol) in a mixture of CS_2 (6 mL)/acetone (2 mL) was stirred at room temperature 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**. Yield: 110.5 mg, 87%. Anal. Calcd for $C_{37}H_{30}AuNP_2S_3$: C, 52.67; H, 3.58; N, 1.66; S, 11.40. Found: C, 52.52; H, 3.68; N, 1.68; S, 11.30. Mp: 202 °C. ^{13}C NMR (DMSO-*d*$_6$/TMS): 251.6 (CS_3) ppm. IR (cm^{-1}): 940, 927, 910.

Reaction of 1 with Iodine. A solution of iodine (27 mg, 0.11 mmol) in dichloromethane (15 mL) was added dropwise to a stirred suspension of **1** (180 mg, 0.11 mmol) in dichloromethane (5 mL). A cloudy red solution formed, which was filtered through Celite and concentrated to *ca.* 5 mL. Diethyl ether (10 mL) was added to precipitate **2** as a yellow-orange solid, which was filtered off, washed with diethyl ether (6 mL), and dried in a nitrogen stream. Yield: 179 mg, 86%. Anal. Calcd for $C_{37}H_{30}AuINP_2S_3$: C, 45.78; H, 3.12; N, 1.44, S, 9,91. Found: C, 45.75; H, 3.06; N, 1.46; S, 9.67. Dec pt: 138 °C. Λ_M (acetone, 5.06×10^{-4} M): 219.4 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(C=S), 1066; ν(C−S), 842; ν(Au−S), 380. Mass spectrum (FAB$^-$) [*m*/*z* (% abundance)]: 534 ($Au_2CS_4^-$, 8), 450 (AuI_2^-, 11), 349 ($AuC_2S_4^-$, 78), 163 (100). **2** proved to be an equimolar mixture of $[(PPh_3)_2N][Au(CS_3)_2]$ and $[(PPh_3)_2N][AuI_2]$ (see below).

$[(PPh_3)_2N][Au(CS_3)_2]$ (3). Solid PTo_3 (78 mg, 0.26 mmol) was added to a red solution of **2** (500 mg, 0.26 mmol) in dichloromethane (15 mL). The resulting orange solution was stirred for 0.5 h and concentrated (6 mL). Addition of diethyl ether (12 mL) gave a bright orange precipitate, which was filtered off, washed with methanol (10 × 2 mL) and diethyl ether (3 × 2 mL), and dried in a nitrogen stream. Yield: 219 mg, 89%. Anal. Calcd for $C_{38}H_{30}AuNP_2S_6$: C, 47.95; H, 3.18; N, 1.47; S, 20.21. Found: C, 47.78; H, 3.09; N, 1.48; S, 20.10. Mp: 136 °C. Λ_M (acetone, 5.0×10^{-4} M): 100 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(C=S) 1066; ν(C−S) 862, 850, 842; ν(Au−S) 380. ^{13}C-{^1H} NMR (75 MHz, $CDCl_3$, δ): 236.0 (s, CS_3). Mass spectrum (FAB$^-$): [*m*/*z* (% abundance)]: 342 (32), 413 ($[Au(CS_3)_2]^-$, 59), 482 (41), 495 (57).

$[(PPh_3)_2N][Au^{I}_n\{Au^{III}(CS_3)_2\}_{n+1}]$ (4). To a solution of **2** (900 mg, 0.46 mmol) in dichloromethane (15 mL) was added methanol (30 mL). Immediately, a fine red precipitate formed, which was stirred for 1.5 h and separated by centrifugation. The product was washed with methanol (15 mL) and diethyl ether (15 mL) and dried at 60 °C for 12 h. Yield: 290 mg, 88%. Anal. Calcd for $C_{50}H_{30}Au_{13}NP_2S_{42}$ ($n = 6$): C, 13.02; H, 0.66; N, 0.30, S, 29.18. Found: C, 12.96; H, 0.55; N, 0.21; S, 29.97. Dec pt: 230 °C. IR (cm^{-1}): ν(C=S), 1024; ν(Au^{III}−S), 374; ν(Au^{I}−S), 268. In the mass spectrum (FAB$^-$) no peaks are observed in the range *m*/*z* 100−1400.

$[Au(S_2CNEt_2)_2][Au(CS_3)_2]$ (5). A solution of $[Au(S_2CNEt_2)_2]ClO_4$ (59 mg, 0.10 mmol) in acetone (25 mL) was added dropwise to a stirred solution of **3** (95 mg, 0.10 mmol) in acetone (25 mL). The resulting orange precipitate of **5** was filtered off, washed with acetone (3 × 3 mL) and diethyl ether (2 mL), and air dried. Yield: 72 mg, 79%. Anal. Calcd for $C_{12}H_{20}Au_2N_2S_{10}$: C, 15.89; H, 2.22; N, 3.09; S, 35.36.

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Table 1. Crystal Data for Complex **6**

molecular formula	$C_{37}H_{30}AuCl_2NP_2S_3$
M_r	914.61
space group	$P\bar{1}$
a (Å)	9.482(2)
b (Å)	11.888(2)
c (Å)	17.303(2)
α (deg)	108.236(6)
β (deg)	93.340(10)
γ (deg)	95.605(10)
V (Å^3)	1835.5(5)
Z	2
T (K)	173(2)
λ (Å)	0.710 73
ρ_{calc} (Mg/m^3)	1.655
F(000)	900
μ (mm^{-1})	4.439
indepdt reflcns	6344
params	415
restraints	354
R1[a]	0.0393
wR2[b]	0.0970
$S(F^2)$	1.064
max $\Delta\rho$ (e Å^{-3})	1.783

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ for reflections with $I > 2\sigma I$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\ ]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and a and b are constants set by the program.

Found: C, 15.87; H, 2.13; N, 3.07; S, 35.52. Dec pt: 127−133 °C. Λ_M (acetone, 2.2×10^{-4} M): 100 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(C−N), 1538; ν(C═S), 1048; ν(C−S), 862, 846; ν(Au−S), 380. Mass spectrum (FAB$^-$) [m/z (% abundance)]: 494 ($[Au(S_2CNEt_2)_2]^-$, 7), 413 ($[Au(CS_3)_2]^-$, 7).

$[(PPh_3)_2N][AuCl_2(CS_3)]$ (6). A solution of $PhICl_2$ (83 mg, 0.30 mmol) in dichloromethane (15 mL) was added dropwise to a solution of **3** (286 mg, 0.30 mmol) in dichloromethane (15 mL). The resulting orange-red cloudy solution was filtered through Celite and concentrated (10 mL). Addition of diethyl ether (30 mL) gave a small amount of $[(PPh_3)_2N][AuCl_2]$ as a white precipitate which was removed by filtration. On storage of the clear orange solution in the refrigerator for 12 h, orange plates of **6** formed. Yield: 215 mg, 78%. Anal. Calcd for $C_{37}H_{30}AuCl_2NP_2S_3$: C, 48.59; H, 3.31; N, 1.53; S, 10.52. Found: C, 48.62; H, 3.24; N, 1.55; S, 10.23. Dec pt: 117 °C. Λ_M (acetone, 5.4×10^{-4} M): 115 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(C═S), 1090; ν(C−S), 836; ν(Au−S), 362; ν(Au−Cl), 332, 310.

Crystal data: $C_{37}H_{30}AuCl_2NP_2S_3$, triclinic, space group $P\bar{1}$, a = 9.482(2) Å, b = 11.888(2) Å, c = 17.303(2) Å, α = 108.236(6)°, β = 93.340(10)°, γ = 95.605(10)°, V = 1835.5 Å^3, Z = 2, D_x = 1.655 Mg m^{-3}, λ(Mo Kα) = 0.710 73 Å, μ = 4.44 mm^{-1}, F(000) = 900, T = −100°C. *Data collection and reduction*: An orange lath ca. $0.8 \times 0.25 \times 0.08$ mm was mounted on a glass fiber in inert oil and transferred to the cold gas stream of a Siemens R3 diffrectometer. A total of 6757 reflections were registered to $2\theta_{max}$ 50°, of which 6344 were independent. An absorption correction based on ψ-scans gave transmissions of 0.664−1.000. *Structure solution and refinement*: The structure was solved by the heavy-atom method and refined anisotropically on F^2 using the program SHELXL-93 (G. M. Sheldrick, University of Göttingen). Local ring geometry and U components of neighboring atoms were subjected to 354 restraints. H atoms were included using a riding model. The final w$R(F^2)$ was 0.097, with conventional $R(F)$ 0.039, for 415 parameters (max $\Delta\rho$ = 1.8 e Å^{-3}; $S(F^2)$ = 1.06). Tables 1 and 2 give crystallographic data and selected bond lengths and angles.

$[(PPh_3)_2N][AuBr_2(CS_3)]$ (7). To a solution of **6** (92 mg, 0.10 mmol) in acetone (8 mL) was added solid NaBr (40 mg, 0.39 mmol). The resulting clear red solution was stirred for 2 h and the solvent evaporated to dryness. The remaining residue was extracted with dichloromethane (8 mL), and the extract was filtered through Celite to remove NaCl and NaBr. The red filtrate was concentrated (4 mL), and diethyl ether (20 mL) was added to precipitate a small amount of $[(PPh_3)_2N][AuBr_2]$, which was removed by filtration. On storage of the mother liquor in the refrigerator for 12 h, dark red needles of **7** formed. Yield: 55 mg, 55%. Anal. Calcd for $C_{37}H_{30}AuBr_2NP_2S_3$: C, 44.28; H, 3.01; N, 1.40; S, 9.58. Found: C, 44.39; H, 2.99; N, 1.43; S, 9.56. Dec pt: 103 °C. Λ_M (acetone, 5.4×10^{-4} M): 111 $^{-1}$ cm^2 mol^{-1}. IR (cm^{-1}): ν(C═S), 1086; ν(C−S), 850, 830; ν(Au−Br), 252.

$[(PPh_3)_2N][AuI_2(CS_3)]$ (8). Solid iodine (30 mg, 0.12 mmol) was added to a solution of **3** (110 mg, 0.12 mmol) in dichloromethane (6 mL), resulting in an orange-red suspension that became a dark red cloudy solution on stirring for 40 min. This solution was then filtered through Celite and concentrated (5 mL). Diethyl ether (30 mL) was added to precipitate $[(PPh_3)_2N][AuI_2]$ as an orange-brown solid, which was removed by filtration. On storage of the dark red filtrate in the refrigerator for 12 h, red-violet needles of **8** formed. Yield: 73 mg, 55%. Anal. Calcd for $C_{37}H_{30}AuI_2NP_2S_3$: C, 40.49; H, 2.76; N, 1.28; S, 8.76. Found: C, 40.94; H, 2.78; N, 1.28; S, 8.63. Dec pt: 94°C. Λ_M (acetone, 5.0×10^{-4} M): 111 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(C═S), 1074; ν(C−S), 846; ν(Au−S), 378.

$[Au(CS_3)(phen)]CF_3SO_3$ (9). To a solution of **6** (92 mg, 0.10 mmol) in acetone (8 mL) were added 1,10-phenanthroline−water (20 mg, 0.10 mmol) and $Tl(CF_3SO_3)$ (71 mg, 0.20 mmol). An orange solid and a pink solution formed instantly. After decantation of the solution, the solid was treated with acetone (10×4 mL) and the extracts, combined with the first solution, were filtered through Celite to give a clear pink solution. Evaporation of the solvent to *ca.* 10 mL led to the precipitation of **9** as a pink solid, which was filtered off, washed with acetone (2×2 mL) and diethyl ether (5 mL), and dried in a nitrogen stream. Yield: 33 mg, 52%. Anal. Calcd for $C_{14}H_8AuF_3N_2O_3S_4$: C, 26.50; H, 1.27; N, 4.42; S, 20.22. Found: C, 26.54; H, 1.21; N, 4.32; S, 20.17. Dec pt: 156 °C. Λ_M (acetone, 3.8×10^{-4} M): 115 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(C═S), 1100.

$[Au(CS_3)(bipy)]CF_3SO_3$ (10). This complex was prepared as described for **9**, starting from **6** (101 mg, 0.11 mmol), 2,2′-bipyridyl (17 mg, 0.12 mmol), and $Tl(CF_3SO_3)$ (78 mg, 0.22 mmol). A pink solid was obtained. Yield: 20 mg, 30%. Anal. Calcd for $C_{12}H_8AuF_3N_2O_3S_4$: C, 23.61; H, 1.32; N, 4.59; S, 21.01. Found: C, 23.25; H, 1.15; N, 4.47; S, 20.97. Dec pt: 163°C. Λ_M (acetone, 3.7×10^{-4} M): 122 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(C═S), 1092.

Results and Discussion

A solution of $[(PPh_3)_2N][Au(SH)_2]$ in a mixture of CS_2 and acetone forms an orange-yellow precipitate of $[(PPh_3)_2N]_2[Au_2(CS_3)_2]$ (**1**). The crystal structure and other properties of **1** have been reported (see Scheme 1).[27] Complex **1** is the first (trithiocarbonato)gold complex and also the first containing a μ^2-η^2-bridging CS_3 ligand (see **F** in Chart 1). Although sodium or potassium salts of CS_3^{2-} can be obtained by treating the corresponding hydrosulfides with CS_2,[29] this is the first time, as far as we are aware, that a trithiocarbonate complex is the sole product of the reaction of CS_2 with a (hydrosulfido)metal complex. The two only precedents for such a reaction led to a mixture of compounds ($[Ni^IL_3(SH)] + CS_2 \rightarrow [Ni^{II}L_3(CS_3)] + [Ni^0L_3(CS_2)] + ...$)[5b] or to a dithioformate complex, arising from CS_2 insertion into the metal−hydrogen, rather than the metal−sulfur, bond ($[Cp^*IrH(SH)(L)] + CS_2 \rightarrow [Cp^*Ir\{SC(S)H\}(SH)(L)]$).[30]

We have unsuccessfully attempted the syntheses of trithiocarbonato complexes of gold(I) and gold(III) from Q_2CS_3 (Q = K, Tl). The reaction of K_2CS_3 with $[(PPh_3)_2N][AuCl_2]$ (1:1) in MeOH gives an orange-brown precipitate, the IR spectrum of which shows the characteristic bands of **1**. However the analytical data differ from those calculated for **1**, suggesting that other (inseparable) compounds are present in the reaction mixture. When the same reaction is attempted in acetone, the starting materials are recovered unchanged, probably because of the insolubility of K_2CS_3 in this solvent. $[AuClPPh_3]$ or $[Au_2Cl_2(dppm)]$ react with K_2CS_3 in MeOH giving, respectively, $[(AuPPh_3)_2(\mu_2\text{-}S)]$ (by IR and ^{31}P NMR) or $[\{Au_2(dppm)\}(\mu_2\text{-}S)]_n$ (by IR and elemental analysis). $[(PPh_3)_2N][AuCl_4]$ reacts with K_2CS_3 (1:2 in MeOH) to give an insoluble brown mixture in which only the gold(I) complex **1** has been identified

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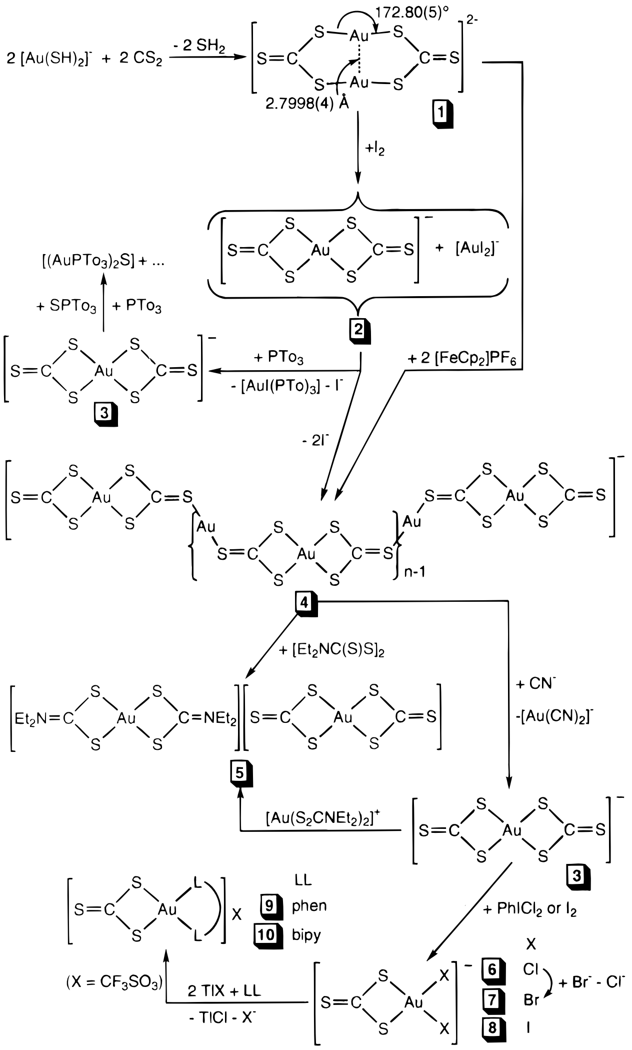
(30) Klein, D. P.; Kloster, G. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 2022.

Scheme 1



(by IR), indicating that a reduction process has taken place. $[(PPh_3)_2N][AuCl_4]$ does not react with Tl_2CS_3 in dichloromethane probably because of the insolubility of the latter. Therefore, although trithiocarbonato salts have been used in the synthesis of many trithiocarbonato complexes,[5a,9b,c,10,12,14,16,19a,21a,d,22a,24,26] the method seems unsuited to the synthesis of (trithiocarbonato)gold derivatives.

We thought it of interest to explore the use of complex **1** as a precursor for binuclear (trithiocarbonato)gold(II) complexes, given that many binuclear gold(I) complexes are known to undergo oxidative addition with halogens, pseudohalogens, or alkyl halides to give gold(II) complexes containing a gold–gold bond.[31] In some cases mixed-valence gold(III)–gold(I) complexes are obtained. Thus, the dimeric gold(I) dialkyldithiocarbamates, $[Au_2(S_2CNR_2)_2]$,[32] and the structurally related anionic complex $[Au_2(i\text{-MNT})_2]^{2-}$ (i-MNT = $[S_2CC(CN)_2]^{2-}$)[33] react with 1 equiv of halogen to give binuclear gold(II) complexes that, in the case of $[Au_2(i\text{-MNT})_2X_2]^{2-}$, can be isolated at low temperatures. At room temperature these complexes undergo disproportionation yielding mixed-valence salts $[Au^{III}(S_2CNR_2)_2][Au^{I}X_2]$ or a mixture of $[Au^{III}(i\text{-MNT})_2]^-$ and $[Au^{I}X_2]^-$, respectively. In our case, slow addition of a solution of $PhICl_2$ to a suspension of **1** (1:1), both in dichloromethane at −78°C, gave instead an insoluble black solid that we could not identify. Under the same conditions, **1** reacts with I_2 to give a black solid and a dark green solution—probably containing the required gold(II) complex—that upon warming to −40 °C becomes red. We could identify neither the black solid nor the mixture of compounds obtained from the red solution.

However, at room temperature, **1** reacts with iodine (1:1) in dichloromethane to give a red solution. If the reaction mixture is concentrated and diethyl ether added, an orange crystalline solid (**2**) is obtained, the elemental analyses and IR spectrum of which are the same as those of an equimolar mixture of the gold(III) complex $[(PPh_3)_2N][Au(CS_3)_2]$ (**3**) (see below) and $[(PPh_3)_2N][AuI_2]$ (see Scheme 1). In the Debye–Scherrer powder diagrams of **2** and of an equimolar mixture of **3** and $[(PPh_3)_2N][AuI_2]$ no significant differences are observed. Therefore, the homogeneous crystalline solid **2** is likely to be the result of cocrystallization of $[(PPh_3)_2N][Au(CS_3)_2]$ and $[(PPh_3)_2N][AuI_2]$. Similarly, the room-temperature reaction of equimolar amounts of **1** and $PhICl_2$ in dichloromethane gives a mixture (**2′**) of **3** and $[(PPh_3)_2N][AuCl_2]$ analogous to **2** (by IR). Therefore, all our attempts to obtain gold(II) complexes from **1** by oxidative addition of X_2 (X = Cl, I) at room or low temperature failed.

Both **2** and **2′** are unstable in dichloromethane or acetone solutions; after a few minutes (**2′**) or hours (**2**) an insoluble dark-red solid is formed, analyzing as the mixed-valence complex $[(PPh_3)_2N][Au^{I}_{n}\{Au^{III}(CS_3)_2\}_{n+1}]$ (**4**) with an average n value of 6 (see Scheme 1). Addition of methanol accelerates these processes. The polymeric species **4** was also obtained when **2** was stirred with methanol in an attempt to separate its two components. The formation of **4** could be interpreted as the result of the substitution of the chloro or iodo ligands in $[(PPh_3)_2N][AuX_2]$ by the CS_3 ligands of complex **3**. The structure of **4** could consist of alternating anions $[Au^{III}(CS_3)_2]^-$ and Au^+ cations to give a polymeric chain with two terminal $Au(CS_3)_2$ units (see Scheme 1). The following data also support our proposal for the nature of **4**: (i) By reaction of **3** with $[(PPh_3)_2N][AuCl_2]$ or $[(PPh_3)_2N][AuI_2]$ or with $[Au(tht)_2]CF_3SO_3$, complex **4** is obtained, whereas the more stable $[Au(CN)_2]^-$ or $[Au(C_6F_5)_2]^-$ complexes do not react with **3**; impure **4** is also obtained by oxidizing the gold(I) complex **1** with $[FeCp_2]PF_6$ (1:2). (ii) **4** dissolves in acetone in the presence of NaCN to give a yellow solution from which, upon addition of $[(PPh_3)_2N]Cl$, a mixture of **3** and $[(PPh_3)_2N][Au(CN)_2]$ is obtained. (iii) The reaction of **4** with tetraethylthiuram disulfide, $[Et_2NC(S)S]_2$, gives the new complex $[Au(S_2CCNEt_2)_2][Au(CS_3)_2]$ (**5**) which is the result of the oxidation of Au(I) to Au(III) by the disulfide; complex **5** can also be obtained by reacting **3** with $[Au(S_2CNEt_2)_2]ClO_4$ (see Scheme 1). We have observed that washing **4** repeatedly with dichloromethane causes its color to darken and lowers its sulfur content. This could be interpreted as a consequence of the formation of small amounts of Au_2S or Au_2S_3 with loss of CS_2.

The best method to prepare $[(PPh_3)_2N][Au(CS_3)_2]$ (**3**) is by reacting **2** with PTo_3 (To = C_6H_4Me-4) in a 1:1 molar ratio. The byproducts $[AuI(PTo_3)]$ and $[(PPh_3)_2N]I$ can be easily separated and were identified by elemental analyses, $[(PPh_3)_2N]I$, or ^1H and ^{31}P NMR, $[AuI(PTo_3)]$. Although PTo_3 also reacts with complex **3** [2:1; to give $[(AuPTo_3)_2S]$ and $S{=}PTo_3$], this reaction must be slower than that with $[(PPh_3)_2N][AuI_2]$ to give $[AuI(PTo_3)]$ and $[(PPh_3)_2N]I$ and does not interfere the synthesis of **3**.

The reaction of complex **3** and $PhICl_2$ (1:1) gives $[(PPh_3)_2N][AuCl_2(CS_3)]$ (**6**) (see Scheme 1). Alternatively, **6** can be obtained by reacting **1** with $PhICl_2$ (1:2) in diethyl ether. The complex $[(PPh_3)_2N][AuBr_2(CS_3)]$ (**7**) can be obtained by reacting

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(31) Fackler, J. P., Jr. *Polyhedron* **1997**, *16*, 1.

(32) Calabro, D. C.; Harrison, B. A.; Palmer, G. T.; Moguel, M. K.; Rebbert, R. L.; Burmeister, J. L. *Inorg. Chem.* **1981**, *20*, 4311.

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6 with excess of NaBr. Similarly, iodine reacts with **3** (1:1) in dichloromethane to give $[(PPh_3)_2N][AuI_2(CS_3)]$ (**8**) in high yield. Coucouvanis and Fackler have described the preparation of $(BzPh_3P)_2[Ni(CS_4)_2]$ (Bz = $PhCH_2$) using K_2CS_4 or by oxidation of $(BzPh_3P)_2[Ni(CS_3)_2]$ with iodine or with sulfur.[21b] Although the sulfur addition accomplishes the conversion quantitatively, the iodine oxidation leads to *ca.* 50% conversion, and the reaction mechanism has not been ascertained. In our case, no (perthiocarbonato)gold species could be detected and we suggest that, upon oxidation of one of the CS_3^{2-} ligands, the created vacancies are occupied by two iodide anions to give **8**. Complexes **6**−**8** are light sensitive and decompose in the solid state or in solution to give the corresponding $[(PPh_3)_2N][AuX_2]$ complexes. According to their decomposition points, the thermal stability decreases in the series **6** > **7** > **8**.

Cationic complexes $[Au(CS_3)(LL)]CF_3SO_3$ [LL = 1,10-phenanthroline (phen) (**9**), 2,2′-bipyridyl (bipy) (**10**)] can be obtained by reacting **6** with TlO_3SCF_3 and the corresponding bidentate ligand (1:2:1) in acetone (see Scheme 1). Both cationic complexes are poorly soluble in acetone and precipitate together with the TlCl from which they can be separated by extracting the mixture repeatedly with the same solvent. **9** and **10** dissolve in dimethyl sulfoxide giving pink-violet solutions which decompose in a few minutes to give unidentified brown species. Although complexes **9** and **10** in the solid state are also very unstable and decompose after 24 h at room temperature, they can be stored at −20 °C. All attempts to prepare cationic complexes with different ligands [γ-picoline, *N,N,N′,N′*-tetramethylethylenediamine, neocuproin, or $SP(Ph)_2CH_2P(Ph)_2S$)] using the same method failed because of the instability of the pink or violet products formed.

Because of the insolubility (**4**, **5**) or instability (**6**−**10**) of most complexes, only the ^{13}C NMR spectra of **1** and **3** have been measured, showing CS_3 resonances [δ (referred to TMS): **1**, 251.6 ppm (**1**, dmso-d_6); **3**, 236.0 ($CDCl_3$) ppm] that agree with the very few previous results.[6,7b]

The IR spectra of all trithiocarbonato complexes here described show bands due to the CS_3 ligand (see Experimental Section). Most trithiocarbonate complexes[7b,10,18,20a,34] show strong $\nu(C{=}S)$ bands in the range 1050−990 and medium-intensity $\nu(C{-}S)$ at around 850 cm^{-1}, which is the case for complexes **3**−**10**. The spectrum of **1** shows three bands at 940, 927, and 910 cm^{-1}. The energy of the $\nu(C{=}S)$ band decreases in the sequence **10** > **9** > **6** > **7** > **8** > **3** > **5** > **4** > **1**, the wavenumbers being higher by 2−40 cm^{-1} for the cationic complexes **9** and **10** than the anionic ones (**3**, **5**−**8**). In the anionic complexes **6**−**8** the energy of this band increases in the order I < Br < Cl. These data imply that the strength of the C=S bond increases with the electronegativity of the moiety to which the CS_3 ligand is attached, which could reasonably be attributed to the increase in the $p_\pi(S)-p_\pi(C)$ bond component. According to the value of $\nu(C{=}S)$ in **3**, the CS_3 ligand is less electronegative than the halogens. The position of the $\nu(C{=}S)$ band in **4** can be related to the proposed structure because in this case the coordination of the CS_3 ligand to both gold(III) and gold(I) centers must diminish the $p_\pi(S)-p_\pi(C)$ bond component.

The $\nu(Au{-}S)$ stretching mode can only be assigned in some cases (see Experimental Section), and the corresponding band appears in the range 362−380 cm^{-1}.[28] Two $\nu(Au{-}Cl)$ bands appear in the spectrum of **6** at 332 and 310 cm^{-1}, whereas the analogous bromo derivative **7** shows only one band (at 252 cm^{-1}) assignable to $\nu(Au{-}Br)$.

Crystal Structure of Complex 6. The crystal structure of **6** (see Figure 1 and Tables 1 and 2) shows planar $[AuCl_2(CS_3)]^-$ anions (sum of the angles around gold 359.93°, mean deviation of all atoms from least-squares plane 0.08 Å) and $[(Ph_3P)_2N]^+$ cations. The planar coordination at the gold atom is distorted by the bite of the CS_3 ligand; the S(2)−Au−S(1) angle is only 74.49(7)°, associated with wider SAuCl and ClAuCl angles [97.26(6), 95.33(7), and 92.85(7)°, respectively]. Despite the difference in metal oxidation states, the AuS bond distances [2.289(2) and 2.300(2) Å] are similar to those found in complex **1** [2.304(2), 2.293(2) Å].[27] The CS_{Au} bond distances are 1.743(7) and 1.748(7) Å, whereas the CS_{exo} bond is much shorter at 1.608(7) Å. The $S_{exo}CS_{Au}$ angles are 126.8(4) and 127.7(4)°, whereas the $S_{Au}CS_{Au}$ angle, again constrained by the chelate ring geometry, is 105.4(4)°. The CS_{exo} bond length and the $S_{Au}CS_{Au}$ angle in **3** are significantly smaller than those in **1** [1.608(7) vs 1.672(6) Å and 105.4(4) vs 125.9(3)°, respectively], consistent with the strengthening of the $S_{exo}C$ bond as stated above and the chelating coordination of the CS_3 ligand, respectively. In the few trithiocarbonate complexes studied by X-ray crystallography the $C{-}S_M$ distances are longer than the corresponding $C{-}S_{exo}$ (mean values 1.70 and 1.65 Å, respectively) and the $S_M{-}C{-}S_M$ angles are narrow compared with the corresponding $S_M{-}C{-}S_{exo}$ (mean values 106.5 and 126.7°, respectively) imposed by the chelating coordination of the CS_3 ligand.

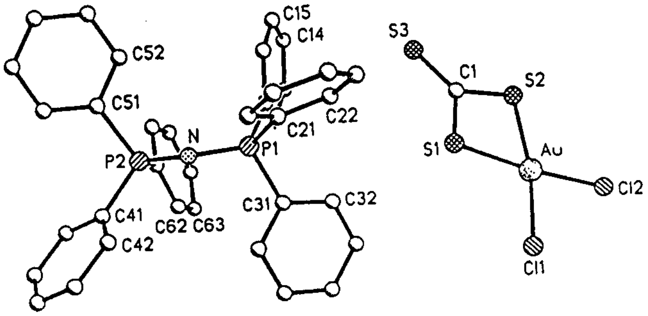

Figure 1. Crystal structure of complex **6**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex **6**

Au−S(1)	2.289(2)	Au−S(2)	2.300(2)
Au−Cl(1)	2.316(2)	Au−Cl(2)	2.329(2)
S(1)−C(1)	1.748(7)	S(2)−C(1)	1.743(7)
S(3)−C(1)	1.608(7)		
S(1)−Au−S(2)	74.49(7)	S(1)−Au−Cl(1)	95.33(7)
S(2)−Au−Cl(1)	169.53(7)	S(1)−Au−Cl(2)	171.66(6)
S(2)−Au−Cl(2)	97.26(6)	Cl(1)−Au−Cl(2)	92.85(7)
C(1)−S(1)−Au	90.1(2)	C(1)−S(2)−Au	89.8(2)
S(3)−C(1)−S(2)	126.8(4)	S(3)−C(1)−S(1)	127.7(4)
S(2)−C(1)−S(1)	105.4(4)		

In the closely related neutral Au^{III} complex ($ClCS_2$-*S,S′*)-$AuCl_2$[35] the geometry at the gold atom is similar to that in **6**, with Au−S 2.317(7), 2.299(5), Au−Cl 2.293(4), 2.304(7) Å, and S−Au−S 75.0(2)°.

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Supporting Information Available: One X-ray crystallographic file, in CIF format, is available. Access information is given on any current masthead page.

IC970478C

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