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FULL PAPER

Gold(I) coordination compounds with mesoionic thiolate ligands and the crystal and molecular structure of bis(1,4,5-trimethyl-1,2,4-triazolium-3-thiolate)gold(I) tetrafluoroborate

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Two-coordinate gold(I) complexes involving mesoionic thiolate ligands have been synthesized, including homoleptic and mixed-ligand complexes. Many of these compounds have stability and solubility properties that are desirable for practical use as gold sensitizers for photographic silver halide dispersions. The crystal structure of bis(1,4,5-trimethyl-1,2,4-triazolium-3-thiolate)gold(I) tetrafluoroborate has been solved by single-crystal X-ray diffraction. Several structural parameters support the view that the mesoionic ligands possess substantial thiolate character as a result of the unusual conjugation present in these heterocyclic compounds.

Introduction

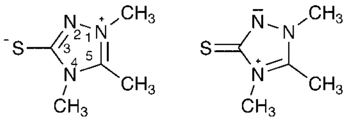
The coordination chemistry of gold(I) is of considerable interest because of the application of gold(I) compounds to treat rheumatoid arthritis[1,2] and, potentially, as anti-cancer drugs.[3] Gold compounds are also important to the photographic industry.[4,5] One of the principal means of increasing the general sensitivity of silver halide microcrystals to light is the process of chemical sensitization during which small quantities of labile sulfur- and gold-containing compounds are digested with the silver halide microcrystals.[6] While the structures of the resulting impurity ion defect sites on the surface of, or inside, the silver halide microcrystals are not known with certainty, it is generally believed that silver sulfide and mixed silver–gold sulfides are formed during chemical sensitization.[7–10]

The design of practical gold(I) sensitizers is subject to rather stringent criteria. The compounds should preferably be soluble to facilitate dispersal in aqueous dispersions of silver halide microcrystals, and most preferably soluble in water to minimize use of organic solvents. The compounds must be stable enough that their solutions have good shelf life for robust use in manufacturing, yet be reactive during chemical sensitization. Among sulfur-donor ligands, experience has shown that thiones and thioureas impart inadequate stability to gold(I). Alkyl or aryl thiolates form oligomers of the general formula Au(SR) that have poor solubility,[11–13] unless solubilizing groups are added.[14,15] Mononuclear complexes $Au(SR)_2^-$ can be made under basic conditions,[11,16,17] but the facile displacement of thiols[18] probably accounts for the formation of the Au(SR) oligomers in many other environments.

Mesoionic thiolates are heterocyclic compounds having unusual delocalization that results in charge separation and substantial thiolate character in the neutral molecules. The intriguing properties of these ligands relative to other sulfur-donors were investigated in a search for more practical gold sensitizers for photographic silver halide microcrystals. The synthesis of two-coordinate gold(I) complexes with mesoionic thiolates and the crystal and molecular structure of bis(1,4,5-trimethyl-1,2,4-triazolium-3-thiolate)gold(I) tetrafluoroborate are reported in this paper. The utility of these gold(I) compounds as photographic sensitizers has been disclosed elsewhere.[19] More recently, Howe[20] has reported another example, chloro(2,3-diphenyl-1,3,4-thiadiazolium-5-thiolate)gold(I).

Results and discussion

Mesoionic compounds are organic heterocycles that possess unusual delocalization of the bonding electrons that cannot be satisfactorily represented by conventional bonding schemes without invoking charge separation.[21] An example of a mesoionic thiolate is 1,4,5-trimethyl-1,2,4-triazolium-3-thiolate **I**.[22] Two alternative Lewis bonding schemes (**IA**,**IB**) for this compound are shown below.



IA **IB**

The high dipole moments measured for mesoionic compounds[23] support the charge separation shown by these representations. Cheung *et al.*[24] have proposed that the bonding in these heterocyclic compounds is best viewed as two separate conjugated systems: one bearing a negative charge comprising the S atom, and the C and N atoms at the 3 and 2 ring positions, respectively, and the other bearing a positive charge comprising the N, C, and N atoms at the 1,5, and 4 positions, respectively. Crystallographic studies of mesoionic thiolates reveal that C–S bond lengths are intermediate between single and double bonds, providing evidence that the compounds possess substantial thiolate character.[24,25]

Reaction of 2 equiv. of **I** with bis(tetramethylthiourea)gold(I) tetrafluoroborate **1** in water yielded bis(1,4,5-trimethyl-1,2,4-triazolium-3-thiolate)gold(I) tetrafluoroborate **2**. Reaction of several other gold(I) precursor compounds with 2 equiv. of **I** afforded the same complex as in **2**, but isolated as different salts **3**, **5**, and **7**. However, reaction of chloroauric acid, instead of a gold(I) precursor compound, with 3 equiv. of **I** gave chloro(1,4,5-trimethyl-1,2,4-triazolium-3-thiolate)gold(I) **8** in 45% yield rather than the homoleptic two-coordinate complex. Analogous iodo- and bromo-complexes **4** and **6** were made by limiting reaction of **I** to 1 equiv. with AuI and $[NBu_4][AuBr_2]$, respectively.

The two-coordinate, mononuclear complex **2** did not show any tendency to lose one ligand to form oligomers in aqueous

Table 1 Selected bond distances (Å) and angles (°) for compound **2**[a]

Au–S1	2.270(4)	N4–C6	1.26(2)
Au–S2	2.274(4)	N5–C7	1.30(2)
S1–C1	1.73(1)	N5–C8	1.49(2)
S2–C6	1.76(1)	N6–C6	1.38(2)
N1–N2	1.39(1)	N6–C7	1.33(2)
N1–C1	1.30(2)	N6–C10	1.47(2)
N2–C2	1.33(2)	C2–C4	1.45(2)
N2–C3	1.46(2)	C7–C9	1.51(2)
N3–C1	1.38(1)		
N3–C2	1.36(2)		
N3–C5	1.47(2)		
N4–N5	1.35(2)		
S1–Au–S2	179.6(2)	Au–S2–C6	100.0(4)
Au–S1–C1	101.4(4)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

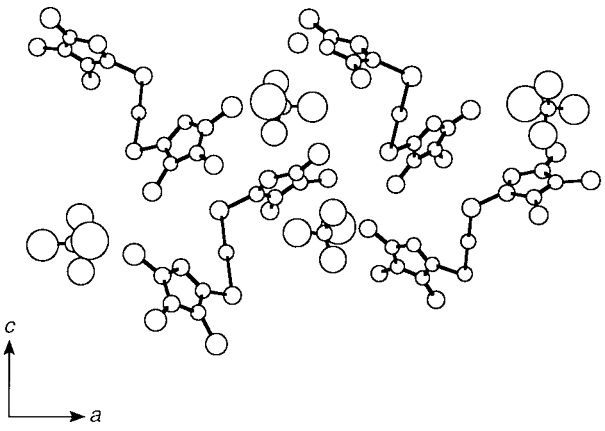


Fig. 1 Unit cell diagram for compound **2**.

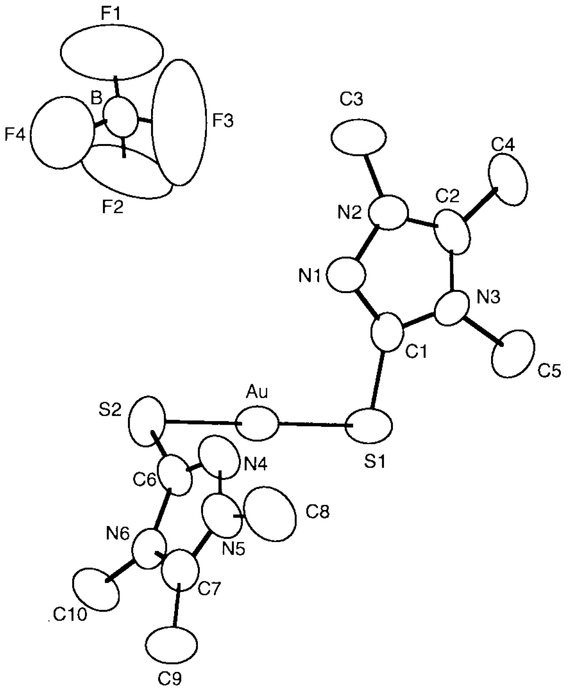


Fig. 2 Molecular structure of compound **2** showing the atomic labelling scheme. Thermal ellipsoids are drawn at the 50% probability level.[26]

solution at moderate pH (3 to 7). Thus the mesoionic thiolates coordinated more strongly to gold(I) than tetramethylthiourea, yet did not display the competing affinity for protons characteristic of alkyl and aryl thiolates.[18]

Other examples of mesoionic ligands employed in the present study to form gold(I) complexes include a number of trisubstituted triazolium thiolates **9**–**14** and one tetrazolium thiolate **15**. Mixed-ligand compounds including phosphine complexes **16**–**18** were also made by reaction of 1 equiv. of a mesoionic thiolate with chloro(trimethylphosphine)gold(I).

The mesoionic thiolate gold(I) compounds are excellent photographic sensitizers and possess good solution stability compared to the tetramethylthiourea complex **1**, as has been previously disclosed.[19] Practical use in silver halide photographic dispersions is facilitated by the good water solubility (0.5 g L^{-1} or more) possessed by many of these compounds, particularly the salts of the cationic, homoleptic complexes.

A single-crystal X-ray structure determination of **2** was carried out in order to examine structural consequences of the unusual delocalization in the mesoionic thiolate as compared to reported structures of gold(I) complexes of thiolates, thioureas, and heterocyclic thiones. The structure of **2** was orthorhombic, space group $Pna2_1$, with $Z = 4$. The unit cell (Fig. 1) contained mononuclear complexes with none of the sub-van der Waals gold–gold interactions that have been observed fairly often for gold(I) compounds.[27,28] The molecular structure is illustrated in Fig. 2 and selected bond distances and angles are listed in Table 1, while crystal and refinement data are given in the Experimental section. The coordination in the complex ion was essentially linear with a S–Au–S angle of 179.6°. The two Au–S bond lengths were within the range reported for many other sulfur-donor ligands (Table 2).

The C–S bond lengths provide an indication of thiolate character in the mesoionic ligands. While the structure of the free ligand**I**has not been determined, the C–S bond lengths in closely related mesoionic thiolates were reported to be intermediate between single and double bond values (1.68–1.69 Å).[24,25] Thus the C–S bond values of 1.73(1) and 1.76(1) Å found in the gold(I) complex **2** probably represent some bond lengthening relative to the free ligand. The slightly longer of these two C–S bonds was rather close to the C–S bond lengths ranging from 1.78 to 1.80 Å that were reported for three homoleptic two-coordinate thiolate complexes of gold(I) (Table 2).[11,17,29] The C–S bond lengths that have been reported for a variety of thiourea and heterocyclic thione complexes of gold(I) (Table 2) generally fall between 1.67 and 1.73 Å. One compound with a C–S bond falling outside this range is bis(thiourea)gold(I) bromide,[30] in which the C–S values were 1.77(1) Å. Interestingly, the Au–S–C bond angles in the latter compound and in **2** were significantly less than those in most other gold(I) compounds referenced in Table 2.

The orientation of the Au–S bond with respect to the planes of the heterocyclic rings may also reflect the extent of thiolate *vs.* thione character in the ligands. If there were substantial C–S double bond character present, the Au–S bond would be orthogonal to both the C–S σ and π bonds and consequently would lie in the ligand plane. In **2**, the AuS$_2$C$_6$N$_4$ torsion angle was 75.2° and the AuS$_1$C$_1$N$_1$ angle was −3.8°. These results suggest that at least one of the mesoionic ligands behaves as a thiolate in the complex **2**, while the second one may retain some thione character.

Lastly, the bond lengths within the heterocyclic rings are worthy of note. Cheung *et al.*[24] based their view of the conjugation in mesoionic compounds in large part upon the intra-ring distances in 1,4,5-triphenyl-1,2,4-triazolium thiolate. In **2**, most of the bond lengths within the rings of each ligand are similar to the corresponding bond lengths reported by Cheung *et al.*[24] However, the C1–N1 bond length (1.30(2) Å) and especially the C6–N4 bond (1.26(2) Å) were even shorter than the 1.328(3) Å reported by Cheung *et al.*[24] for the corresponding atoms at the 3 and 2 ring positions in 1,4,5-triphenyl-1,2,4-triazolium-3-thiolate. These short C–N bond lengths compared to the 1.38(2) Å observed for both C6–N6 and C1–N3 (3 and 4 positions) suggest that structural representation **IA** for the

Table 2 Bond distances and angles in gold(I) complexes with sulfur-donor ligands

Compound	Au–S/Å	C–S/Å	Au–S–C/°	Ref.
2	2.270(4), 2.274(4)	1.73(1), 1.76(1)	101.4(4), 100.0(4)	This work
$[P(C_6H_5)_4][Au(SC_6H_5)_2]$	2.271(8), 2.262(8)	1.79(1), 1.80(1)	107.6(7), 108.9(6)	17
$[NH_4][2,4,6\text{-}iPr_3C_6H_2S)_2Au]$	2.288(4)	1.78(1), 1.80(1)	102.8(5), 107.1(5)	11
$[NEt_4][Au(SAd)_2]$[a]	2.298(4)	1.80(1)	106.0(4)	29
$[Au(Tu)_2]Br$[b]	2.291(4)	1.771(13)	101.4(4)	30
$[Au(Me_2Tu)_2]ClO_4$[c]	2.289(3)	1.728(7)	104.8(3)	31
$[Au(Et_2Tu)_2]ClO_4$[d]	2.293(9), 2.271(9)	1.70(3), 1.67(3)	107(1), 108(1)	31
$[BrAu(Me_4Tu)]$[e]	2.265(2)	1.727(9)	109.6(3)	32
$[ClAu(Et_2BzTu)]$[f]	2.258(3)	1.70(1)	106.9(3)	33
$[Au(Imt)_2]Cl\cdot H_2O$[g]	2.279(8), 2.278(9)	1.713(22), 1.723(20)	111.2(7), 109.8(8)	34
$[ClAu(EtImt)]$[h]	2.25(1)	1.74(2)	106(1)	35
$[ClAu(PrImt)]$[i]	2.26(1)	1.67(1)	107(1)	36
$[Au(PrImt)_2]Cl$[i]	2.283(3), 2.291(3)	1.70(1), 1.73(1)	107.0(4), 106.5(5)	37
$[Au(C_3H_5NS_2)_2]Cl\cdot H_2O$[j]	2.281(5), 2.288(5)	1.735(4), 1.716(14)	106.6(5), 101.9(5)	38
$[Au(C_5H_5NS)_2]ClO_4$[k]	2.278(2)–2.291(3)	1.714(10)–1.739(10)	104.8(4)–107.5(4)	39
$[Au(Tzt)_2]Cl$[i]	2.277(3)	1.715(11)	105.3(4)	40

[a] SAd = adamantyl thiolate. [b] Tu = thiourea. [c] Me_2Tu = 1,3-dimethylthiourea. [d] Et_2Tu = 1,3-diethylthiourea. [e] Me_4Tu = tetramethylthiourea. [f] Et_2-BzTu = *N*,*N*-diethyl-*N*′-benzoylthiourea. [g] Imt = imidazolidine-2-thione. [h] EtImt = *N*-ethylimidazolidine-2-thione. [i] PrImt = *N*-propylimidazolidine-2-thione. [j] $C_3H_5NS_2$ = 1,3-thiazolidine-2-thione. [k] C_5H_5NS = pyridine-2-thione. [l] Tzt = 4-amino-3-methyl-1,2,4-Δ^2-triazoline-5-thione.

ligand does indeed play an important role in forming the gold(I) complex **2**.

Experimental

Chemicals

Chemicals obtained from commercial sources were used without further purification. $HAuCl_4\cdot 3H_2O$ and AuI were obtained from Johnson Matthey, and $ClAuPMe_3$ was from Strem. Tetramethylthiourea, pentamethylene sulfide, 2,2′-thiodiethanol, and HBF_4 (48% aq) were all obtained from Aldrich. $[N(n\text{-}Bu)_4][AuBr_2]$,[41] bis(pentamethylenesulfide)gold(I) tetrafluoroborate,[42] and the mesoionic thiolates[22] were prepared as described in the literature.

^1H NMR spectra were recorded on a Varian VXR-300S spectrometer at 300 MHz. Chemical shifts in D_2O (Cambridge Isotopes) were referenced to an internal standard of 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid, sodium salt (Aldrich).

Synthesis of gold(I) compounds

Bis(tetramethylthiourea)gold(I) tetrafluoroborate 1. Compound **1** was made by a modification of a procedure developed by G. H. Hawks and W. W. White of these laboratories. Tetramethylthiourea (0.327 g; 2.47 mmol) was suspended in 10 mL water and treated, dropwise, with a solution of $HAuCl_4\cdot 3H_2O$ (0.255 g; 0.647 mmol) in 5 mL of water. A gummy orange precipitate formed immediately, quickly turned dark red, and dissolved with gentle warming and stirring. When a clear, colorless solution was formed, 0.2 mL HBF_4 (49% aq) was added and soon white platelets formed. After further cooling to 5 °C, 0.297 g of the product was filtered and dried, 84% yield. Found (calc. for $AuS_2C_{10}H_{24}N_4BF_4$): C, 22.17 (21.91); H, 4.46 (4.41); N, 10.14 (10.22); S, 11.65 (11.70%). ^1H NMR (D_2O): δ 3.257.

Bis(1,4,5-trimethyl-1,2,4-triazolium-3-thiolate)gold(I) tetrafluoroborate 2. A solution of **1** (0.228 g; 0.416 mmol) in 4 mL water, which was prepared by heating to *ca.* 60 °C, was added dropwise to a solution containing the mesoionic thiolate **I** (0.126 g; 0.874 mmol) in 4 mL water. A white precipitate soon began to deposit. The solution was stirred for an additional 5 min after the addition was complete, and then cooled at 5 °C for several hours. The product was then filtered, washed with ethanol, and dried under vacuum to give 0.203 g of white powder, (86% yield). The product was recrystallized from warm water. Found (calc. for $AuS_2C_{10}H_{18}N_6BF_4$): C, 20.87 (21.06); H, 3.13 (3.18); N, 14.71 (14.74); S, 10.87 (11.25%). ^1H NMR (D_2O): δ 3.863, 3.717, and 2.639. Compound **2** was also made in 88% yield by an analogous procedure using bis(pentamethylenesulfide)gold(I) tetrafluoroborate as starting material.

Bis(1,4,5-trimethyl-1,2,4-triazolium-3-thiolate)gold(I) iodide 3. Solid AuI powder (0.256 g; 0.789 mmol) was added slowly to 5 mL of an acetonitrile solution containing **I** (1.578 mmol). The solution developed a yellow-brown color. A small amount of brown precipitate (metallic Au) was filtered off. The solvent was evaporated and the white powder remaining was washed with ethanol and dried to give 0.432 g (90% yield). Found (calc. for $AuS_2C_{10}H_{18}N_6I$): C, 19.58 (19.68); H, 2.94 (2.97); N, 13.56 (13.77); S, 9.69 (10.51%).

Iodo(1,4,5-trimethyl-1,2,4-triazolium-3-thiolate)gold(I) 4. The same reaction procedure as given above for the bis complex **3** was followed except that only one molar equivalent of the mesoionic thiolate **I** was used. After filtering a small amount of metallic gold from the reaction solution, the filtrate was evaporated. The white powder residue was washed with ethanol and dried (85% yield). Found (calc. for $AuSC_5H_9N_3I$): C, 13.30 (12.86); H, 1.95 (1.94); N, 9.17 (9.00); S, 7.51 (6.86%).

Bis(1,4,5-trimethyl-1,2,4-triazolium-3-thiolate)gold(I) bromide 5. $[NBu_4][AuBr_2]$ (0.304 g; 0.508 mmol) was dissolved in 2 mL acetonitrile and added dropwise to 3 mL of an acetonitrile solution containing **I** (1.02 mmol) at about 50 °C. Within a few minutes a white precipitate began to form. After further cooling at −10 °C, 0.257 g white powder was filtered and dried (90% yield). Found (calc. for $AuS_2C_{10}H_{18}N_6Br$): C, 21.07 (21.32); H, 3.19 (3.22); N, 14.62 (14.92); S, 10.56 (11.38%).

Bromo(1,4,5-trimethyl-1,2,4-triazolium-3-thiolate)gold(I) 6. The same procedure as given above for the bis complex **5** was followed except that only one molar equivalent of the mesoionic thiolate **I** was used. The solution was stirred for an hour at about 50 °C, after which the solvent was concentrated until a white precipitate began to form. The white powder was filtered, washed with water and alcohol, and dried (82% yield). The product was recrystallized from hot acetonitrile. Found (calc. for $AuSC_5H_9N_3Br$): C, 14.15 (14.30); H, 2.10 (2.16); N, 9.88 (10.00); S, 7.27 (7.63%).

Bis(1,4,5-trimethyl-1,2,4-triazolium-3-thiolate)gold(I) chloride 7. $HAuCl_4\cdot 3H_2O$ (0.325 g; 0.825 mmol) was converted *in situ* to thiodiethanol gold(I) chloride[43] in 5 mL of a 3 : 1 ethanol–water solution by dropwise addition of neat thiodiethanol (2.48

mmol) and stirring until the solution turned colorless. This reaction solution was, in turn, added dropwise to 2 mL of an aqueous solution containing **I** (1.65 mmol). The solution turned orange, but upon cooling to 5 °C a white precipitate formed (0.310 g, 72% yield). Found (calc. as $AuS_2N_6C_{10}H_{18}Cl$): C, 23.65 (23.15); H, 3.62 (3.50); N, 15.76 (16.20); Cl, 6.67 (6.83); S, 12.04 (12.36%).

Chloro(1,4,5-trimethyl-1,2,4-triazolium-3-thiolate)gold(I) 8. $HAuCl_4\cdot3H_2O$ (0.327 g; 0.831 mmol) was dissolved in 2 mL water and added dropwise to a solution containing 3 molar equiv. of the mesoionic thiolate **I** (2.49 mmol) in 2 mL water. An orange, gummy material precipitated immediately from the clear solution, but subsequently went into solution that also took on an orange color. After stirring a few minutes, a white precipitate formed and 0.14 g of white powder was collected and dried (45% yield). Found (calc. for $AuSC_5H_9N_3Cl$): C, 15.98 (15.99); H, 2.32 (2.42); N, 10.98 (11.19); Cl, 9.43 (9.44); S, 7.86 (8.54%).

Bis(1,5-dimethyl-4-allylmethyl-1,2,4-triazolium-3-thiolate)gold(I) tetrafluoroborate 9. A solution of **1** (0.231 g) in 2 mL water at 60 °C was added dropwise to 3 mL of an aqueous solution of 1,5-dimethyl-4-allylmethyl-1,2,4-triazolium-3-thiolate (0.15 g, 0.886 mmol), also at about 60 °C. After stirring 10 min, the solution was cooled to 5 °C, whereupon colorless platelets formed. The product (0.207 g) was filtered off and dried (79% yield). Found (calc. for $AuS_2C_{14}H_{22}N_6BF_4$): C, 26.96 (27.02); H, 3.54 (3.56); N, 13.59 (13.51); S, 10.03 (10.30%).

Bis(1,5-dimethyl-4-methoxyethyl-1,2,4-triazolium-3-thiolate)gold(I) tetrafluoroborate 10. Solid **1** (0.261 g; 0.476 mmol) was very slowly added to 5 mL of an aqueous solution containing 1,5-dimethyl-4-methoxyethyl-1,2,4-triazolium-3-thiolate (0.178 g; 0.953 mmol). A white precipitate appeared and stirring was continued for a half hour. White powder (0.211 g) was filtered off, washed with ethanol, and dried. A second crop of 0.047 g was obtained after concentrating the filtrate (82% yield total). The compound was recrystallized from hot water. Found (calc. for $AuS_2N_6O_2C_{14}H_{26}BF_4$): C, 25.42 (25.54); H, 3.97 (3.98); N, 12.79 (12.77); S, 8.45 (9.74%).

Bis(1,5-dimethyl-4-amino-1,2,4-triazolium-3-thiolate)gold(I) tetrafluoroborate 11. A solution of **1** (0.215 g; 0.391 mmol) in 3 mL water at 60 °C was added dropwise to 3 mL of an aqueous solution of 1,5-dimethyl-4-amino-1,2,4-triazolium-3-thiolate (0.119 g; 0.822 mmol), also at about 60 °C. Before the addition was completed, a white precipitate began to form. The reaction mixture was stirred an additional 10 min after the addition was complete and then filtered, washed with water and alcohol, and dried. A white powder (0.197 g) was obtained, and a second crop of 0.029 g was recovered by concentrating the filtrate (88% yield total). Found (calc. for $AuS_2C_8H_{16}N_8BF_4$): C, 16.76 (16.79); H, 2.81 (2.82); N, 19.64 (19.58); S, 10.75 (11.21%).

Bis(1,5-dimethyl-4-n-butyl-1,2,4-triazolium-3-thiolate)gold(I) tetrafluoroborate 12. A solution of **1** (0.245 g; 0.447 mmol) in 2 mL water at 60 °C was added dropwise to 2 mL of an aqueous solution of 1,5-dimethyl-4-n-butyl-1,2,4-triazolium-3-thiolate (0.174 g; 0.939 mmol), also at 60 °C. After stirring an additional few minutes, the reaction mixture was allowed to cool whereupon a colorless oil separated. Upon standing at 5 °C overnight the oil crystallized. Semi-crystalline white solid (0.183 g) was filtered off and dried (62% yield). The compound was recrystallized as long needles from boiling water. Found (calc. for $AuS_2C_{16}H_{30}N_6BF_4$): C, 29.28 (29.37); H, 4.53 (4.62); N, 12.81 (12.84); S, 9.66 (9.80%).

Bis(1,5-dimethyl-4-cyclohexyl-1,2,4-triazolium-3-thiolate)gold(I) tetrafluoroborate 13. A solution of **1** (0.198 g; 0.36 mmol) in 3 mL water at 60 °C was added dropwise to a suspension of 1,5-dimethyl-4-cyclohexyl-1,2,4-triazolium-3-thiolate (0.160 g; 0.756 mmol) in 2 mL water at 60 °C. A white precipitate began to form that had a different consistency from the solid thiolate ligand that was initially present. After stirring an additional few minutes, 0.204 g of white powder was filtered off and dried (80% yield). The compound was recrystallized from hot methanol. Found (calc. for $AuS_2C_{20}H_{34}N_6BF_4$): C, 33.71 (34.00); H, 4.77 (4.85); N, 11.83 (11.90); S, 8.75 (9.08%).

Bis(1-methyl-4,5-diphenyl-1,2,4-triazolium-3-thiolate)gold(I) tetrafluoroborate 14. A solution of **1** (0.201 g; 0.367 mmol) was dissolved in 3 mL methanol and added slowly to a partly dissolved suspension of 1-methyl-4,5-diphenyl-1,2,4-triazolium-3-thiolate (0.216 g; 0.806 mmol) in 3 mL methanol. As the addition proceeded, the initial suspension appeared to be taken into solution while a new white precipitate formed. After stirring 10 min, 0.272 g fine white powder was filtered off and dried (91% yield). Found (calc. for $AuS_2C_{30}H_{26}N_6BF_4$): C, 43.92 (44.02); H, 3.24 (3.20); N, 10.30 (10.27); S, 7.43 (7.83%).

Bis(2,3-diphenyl-1,2,3,4-tetrazolium-5-thiolate)gold(I) tetrafluoroborate 15. A solution of **1** (0.226 g; 0.413 mmol) in 3 mL acetone was added dropwise to a partly dissolved suspension of the dark orange 2,3-diphenyl-1,2,3,4-tetrazolium-5-thiolate (0.210 g; 0.826 mmol) in 3 mL refluxing acetone. The solution turned progressively lighter orange in color as the addition proceeded. Near the end of the addition, a yellow precipitate formed. The refluxing suspension was stirred an additional few minutes until all of the solid dark orange specks of the mesoionic thiolate were consumed. The solution was allowed to cool and 0.253 g of fine yellow powder was filtered and dried (77% yield). The material was recrystallized from hot acetonitrile. Found (calc. for $AuS_2C_{26}H_{20}N_8BF_4$): C, 39.85 (39.41); H, 2.79 (2.54); N, 13.85 (14.14); S, 6.83 (8.09%).

(1,4,5-Trimethyl-1,2,4-triazolium-3-thiolate)(trimethylphosphine)gold(I) chloride 16. A solution of the mesoionic thiolate **I** (0.0936 g; 0.652 mmol) in 2 mL water was added slowly to a suspension of $ClAuP(CH_3)_3$ (0.201 g; 0.652 mmol) in 2 mL methanol. As the addition continued, the $ClAuP(CH_3)_3$ was taken into solution. After a few minutes stirring, the solution was filtered of a few remaining particles of the starting compound and then the solvent was evaporated. The residue was redissolved in ethanol but had a cloudy or colloidal appearance until a few drops of water were added to clarify. Ether was added slowly until the cloud point was reached. A flocculant white precipitate formed after standing at −10 °C overnight. White powder (0.187 g) was filtered off and dried, and 0.0184 g was obtained as a second crop (70% yield). Found (calc. for $AuClPSC_8H_{18}N_3$): C, 20.39 (21.27); H, 4.15 (4.02); N, 9.06 (9.30); S, 6.87 (7.10); Cl, 7.88 (7.85%).

(1,4,5-Trimethyl-1,2,4-triazolium-3-thiolate)(trimethylphosphine)gold(I) tetrafluoroborate 17. The reaction procedure given for the chloride salt in the preceding paragraph was followed. After the reaction was complete, approximately 4 molar equiv. of HBF_4 (49% aq.) were added. The solution was concentrated to an oil, which had a slight yellow coloration. The oil was triturated with ethanol, causing it to solidify, and the slightly yellow powder was filtered off and dried (90% yield). It was recrystallized from warm (50 °C) water. Found (calc. for $AuPSC_8H_{18}N_3BF_4$): C, 18.99 (19.10); H, 3.46 (3.61); N, 8.56 (8.35); S, 6.24 (6.37%).

(1,5-Dimethyl-4-allylmethyl-1,2,4-triazolium-3-thiolate)(trimethylphosphine)gold(I) tetrafluoroborate 18. A solution of 1,5-dimethyl-4-allylmethyl-1,2,4-triazolium-3-thiolate (0.177 g; 0.694 mmol) in 2 mL methanol was added dropwise to a suspension of $ClAuP(CH_3)_3$ (0.214 g; 0.694 mmol) in 2 mL

Table 3 Crystallographic parameters for bis(1,4,5-trimethyl-1,2,4-triazolium-3-thiolate)gold(I) tetrafluoroborate **2**

Molecular Formula	$AuS_2N_6C_{10}H_{18}BF_4$
M	570.19
Lattice type	Orthorhombic
Space group	$Pna2_1$
T/°C	23(1)
a/Å	23.121(6)
b/Å	6.567(2)
c/Å	11.971(4)
V/Å^3	1818(2)
Z	4
μ(Mo-Kα)/cm^{-1}	83.4
No. unique reflections measured	2297
No. reflections in refinement ($I > \sigma(I)$)	1946
$R = \Sigma\|F_o\| - K\|F_c\|/\|F_o\|$	0.045
$R_w = [\Sigma w(\|F_o\| - K\|F_c\|)^2/\Sigma w F_o^2]^{1/2}$	0.057

methanol. As the addition proceeded, the solid $ClAuP(CH_3)_3$ was taken into solution. After the addition was completed, 0.3 mL of HBF_4 solution (49% aq.) was added. Concentration of the solution, followed by addition of ether to the cloud point, caused a white precipitate to form, and 0.295 g was filtered off and dried (80% yield). This material was recrystallized from hot ethanol. Found (calc. for $AuSC_{10}H_{20}N_3PBF_4$): C, 22.85 (22.70); H, 3.69 (3.81); N, 8.46 (7.94); S, 6.23 (6.06%).

Single-crystal X-ray structure determination of bis(1,4,5-trimethyl-1,2,4-triazolium-3-thiolate)gold(I) tetrafluoroborate 2

Crystals of **2** were grown from a warm aqueous solution by slow cooling in a Dewar flask. A single crystal was mounted on a glass fiber and data were collected on an Enraf-Nonius CAD4 diffractometer. Programs used in the X-ray study were from the Structure Determination Package (SDP).[44] The structure was solved by the heavy-atom method and refined by the full-matrix least squares method with anisotropic thermal parameters applied in the final cycles. Hydrogen atoms could not be located. The crystal data and refinement parameters are summarized in Table 3. An empirical absorption correction was applied using the program DIFABS.[45] The residual electron density was primarily around the Au and S atoms and the BF_4^- ion.

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References

1 S. T. Crooke, R. M. Snyder, T. R. Butt, D. J. Ecker, H. S. Allaudeen, B. Monia and C. K. Mirabelli, *Biochem. Pharmacol.*, 1986, **35,** 3423.
2 S. P. Fricker, *Transition Met. Chem.*, 1996, **21**, 189.
3 O. M. Ni Dubhghaill and P. J. Sadler, in *Metal Complexes in Cancer Chemotherapy*, ed. B. K. Keppler, VCH, Weinheim, Germany, 1993.
4 F. W. H. Mueller, *Photogr. Sci. Eng.*, 1966, **10**, 338.
5 W. F. Berg, *Gold Bull.*, 1979, **12**, 97.
6 J. M. Harbison, in *The Theory of the Photographic Process*, Macmillan, New York, 4th edn., 1977.
7 H. Kanzaki and Y. Tadakuma, *J. Phys. Chem. Solids*, 1997, **58**, 221.
8 T. Tani, *J. Imaging. Sci. Technol.*, 1998, **42**, 135.
9 L. Dupain-Klerkx and P. Faelens, *J. Photogr. Sci.*, 1987, **35**, 136.
10 M. Kawasaki, T. Yoshiaki and Y. Oku, *J. Imaging. Sci. Technol.*, 1993, **37**, 568.
11 I. Schröter and J. Strähle, *Chem. Ber.*, 1991, **124**, 2161.
12 M. Lotze and M. Bauer, *US Pat.* 5 252 764, 1993.
13 M. A. Mazid, M. T. Razi, P. J. Sadler, G. N. Greaves, S. J. Gurman, M. H. J. Koch and J. C. Phillips, *J. Chem. Soc.*, *Chem. Commun.*, 1980, 1264.
14 B. H. Tavernier and A. J. DeMeyer, *US Pat.*, 3 503 749, 1970.
15 P. Bishop, P. Marsh, A. K. Brisdon, B. J. Brisdon and M. F. Mahon, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 675.
16 G. A. Bowmaker and B. C. Dobson, *J. Chem. Soc.*, *Dalton Trans.*, 1981, 267.
17 P. A. Bates and J. M. Waters, *Acta Crystallogr.*, *Sect. C.*, 1985, **41**, 862.
18 G. E. Coates, C. Kowala and J. M. Swan, *Aust. J. Chem.*, 1966, **19**, 539.
19 J. C. Deaton, *US Pat.*, 5 049 485, 1991 and 5 220 030, 1993.
20 B. P. Howe, *Metal Based Drugs*, 1997, **4**, 273.
21 W. D. Ollis and C. A. Ramsden, in *Advances in Heterocyclic Chemistry*, Academic Press, London, 1976, vol. 19.
22 H. W. Altland, E. L. Dedio and G. J. McSweeney, *US Pat.*, 4 378 424, 1983.
23 A. R. McCarthy and W. D. Ollis, *J. Chem. Soc. B*, 1969, 1185.
24 K.-K. Cheung, A. Echevarria, S. Galembeck, M. A. Maciel, J. Miller, V. M. Rumjanek and A. M. Simas, *Acta Crystallogr.*, *Sect. C*, 1993, **49**, 1092.
25 Y. Kushi and Q. Fernando, *J. Am. Chem. Soc.*, 1970, **92**, 1965.
26 C. K. Johnson, ORTEPII, ORNL-5138 Report, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
27 S. S. Pathaneni and G. R. Desiraju, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 319.
28 M. Nakamoto, W. Hiller and H. Schmidbaur, *Chem. Ber.*, 1993, **126**, 605.
29 K. Fujisawa, S. Imai and Y. Moro-oka, *Chem. Lett.*, 1998, 167.
30 L. C. Porter, J. P. Fackler, J. Costmagna and R. Schmidt, *Acta Crystallogr.*, *Sect. C*, 1992, **48**, 751.
31 R. J. Staples, J. P. Fackler and J. Costamagna, *Acta Crystallogr.*, *Sect. C*, 1997, **53**, 1555.
32 A. C. Fabretti, A. Giusti and W. Malavasi, *J. Chem. Soc.*, *Dalton Trans.*, 1990, 3091.
33 W. Bensch and M. Schuster, *Z. Anorg. Allg. Chem.*, 1992, **611**, 99.
34 P. G. Jones, J. J. Guy and G. M. Sheldrick, *Acta Crystallogr.*, *Sect. B*, 1976, **32**, 3321.
35 M. S. Hussain and A. A. Isab, *Transition Met. Chem.*, 1984, **9**, 398.
36 M. S. Hussain and A. A. Isab, *J. Coord. Chem.*, 1985, **14**, 17.
37 M. S. Hussain and A. A. Isab, *Transition Met. Chem.*, 1985, **10**, 178.
38 P. D. Akrivos, S. K. Hadjikakou, P. Karagiannidis, M. Gdaniec and Z. Kosturkiewicz, *Polyhedron*, 1994, **13**, 753.
39 R. Uson, A. Laguna, M. Laguna, J. Jimenez, M. P. Gomez, A. Sainz and P. G. Jones, *J. Chem. Soc.*, *Dalton Trans.*, 1990, 3457.
40 M. B. Cingi, F. Bigoli, M. Lanfranchi, E. Leporati, M. A. Pellinghelli and C. Foglia, *Inorg. Chim. Acta*, 1995, **235**, 37.
41 P. Braunstein and R. J. H. Clark, *J. Chem. Soc.*, *Dalton Trans.*, 1973, 1845.
42 D. T. Hill, *US Pat.*, 4 165 380, 1979.
43 A. K. Al-Sa'ady, C. A. McAuliffe, R. V. Parish and J. A. Sandbank, *Inorg. Synth.*, 1981, **23**, 185.
44 Structure determination package, version 3.0, Enraf-Nonius Corporation, Delft, Holland, 1985.
45 N. Walker and D. Stuart, DIFABS, *Acta Crystallogr.*, *Sect. A*, 1983, **39**, 158.

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