

Pentafluorophenyl(dithiocarbamate)gold(III) complexes. Crystal and molecular structure of $(C_6F_5)_2Au\{S_2CN(CH_2Ph)_2\}$

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Abstract

Addition of dialkyldithiocarbamate ligands to solutions of $Au(C_6F_5)_3(tht)$ gives either monomeric $Q[Au(C_6F_5)_3(\eta^1-S_2CNR_2)]$ ($Q = N(PPh_3)_2$ or NBu_4 ; $R = Me, Et, CH_2Ph$) or binuclear dithiocarbamate-bridged complexes. $NBu_4[(\mu-S_2CNR_2)\{Au(C_6F_5)_3\}_2]$. When binuclear $[Au(\mu-Cl)(C_6F_5)_2]_2$ is used as gold source, neutral mononuclear complexes $[Au(C_6F_5)_2(\eta^2-S_2CNR_2)]$ are obtained. The structure of $[Au(C_6F_5)_2\{\eta^2-S_2CN(CH_2Ph)_2\}]$ has been determined by X-ray diffraction.

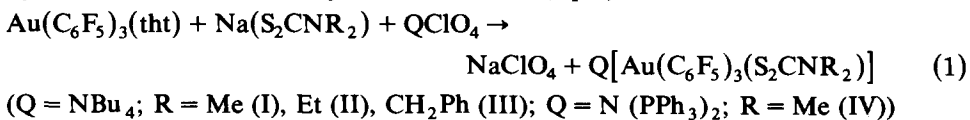
Introduction

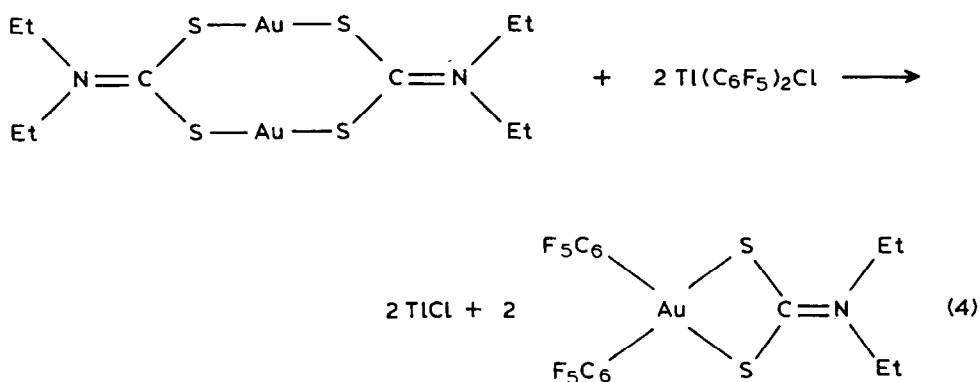
A few dialkylgold(III) *N,N*-dialkyldithiocarbamates have been prepared by the alkylation of the corresponding dihalo derivatives with either Grignard reagents at $-80^\circ C$ or CdR_2 compounds at $0^\circ C$ [1]. No arylgold(III) complexes containing unidentate or bridging dithiocarbamate ligands have been reported previously.

We describe here arylgold(III) complexes containing *N,N*-dialkyldithiocarbamate acting as a unidentate ligand, in $Q[Au(C_6F_5)_3(S_2CNR_2)]$ ($Q = N(PPh_3)_2, NBu_4$; $R = Me, Et, CH_2Ph$), as a bridging ligand, in $NBu_4[(\mu-S_2CNR_2)\{Au(C_6F_5)_3\}_2]$, and as a chelating ligand, in $Au(C_6F_5)_2(S_2CNR_2)$.

Results and discussion

The neutral tetrahydrothiophen (tht) in $Au(C_6F_5)_3(tht)$ can be readily displaced by addition to sodium dialkyldithiocarbamate (eq. 1)





The dialkyldithiocarbamate ligands cleave the chloride bridges in binuclear $[\text{Au}(\mu\text{-Cl})(\text{C}_6\text{F}_5)_2]_2$ and simultaneously displace the chloride ions, to give neutral complexes (eq. 3).

There is a variety of conceivable syntheses of complexes of this type; we have synthesised complex IX by treating *cis*- $[\text{Au}(\text{C}_6\text{F}_5)_2(\text{tht})_2]\text{ClO}_4$, or *cis*- $[\text{Au}(\text{C}_6\text{F}_5)_2(\text{O-ClO}_3)(\text{PPh}_3)]$ with $\text{Na}[\text{S}_2\text{CNEt}_2]$ or by oxidizing $[\text{Au}(\text{S}_2\text{CNEt}_2)]_2$ with $\text{Ti}(\text{C}_6\text{F}_5)_2\text{Cl}$ (eq. 4).

At room temperature, complexes VIII–X are air- and moisture-stable pale yellow solids. They are soluble in dichloromethane, chloroform (monomeric, isopiestic method), diethyl ether and acetone (non-conducting) and slightly soluble in n-hexane.

Their IR spectra show two strong bands at 810 and 800 cm^{-1} , thereby confirming that the two C_6F_5 groups are mutually *cis* [3]. $\nu(\text{CN})$ appears at 1565(vs) (VIII), 1530(vs) (IX) and 1525(vs) (X) cm^{-1} and $\nu(\text{CS})$ at 1240(m) (VIII), 1210(m) (IX) and 1225(s) cm^{-1} (X). The structure of complex X was confirmed by a single-crystal X-ray structure determination (Fig. 1). The atoms C(31), C(41), Au, S(1), S(2), C(99), N(99), C(1) and C(2) all lie in a plane (mean deviation 0.04 Å); the phenyl groups C(11)–C(16) and C(21)–C(26) lie above and below this plane, respectively. The two chemically equivalent halves of the molecule (related to a good approximation by a non-crystallographic two-fold axis passing through Au, C(99) and N(99)) display almost equal bond lengths and angles (maximum difference 3 e.s.d.'s). The C(99)–N(99) bond length of 1.338(9) Å is consistent with considerable multiple bond character.

Several gold(III) complexes with di-*n*-butyldithiocarbamate (dtc) ligands have been investigated by X-ray methods [10]. Some of the structure determinations were of moderate precision, and none involved complexes with Au–C bonds, and so generalized comparisons are difficult. Reported Au–S bond lengths range from 2.289 to 2.357 Å (*trans* to S or Br ligands) and often differing considerably for chemically equivalent bonds in the same molecule. The C–S bond lengths are fairly constant (av. 1.74 Å for 24 bonds). The C–N bond lengths average 1.31 Å, but the e.s.d.'s were mostly in the range 0.02–0.05 Å, again precluding useful discussion. The variation of C–N bond order with the nature of the *trans* ligands at gold has been discussed in terms of the IR frequency of the C–N bond [1], but more

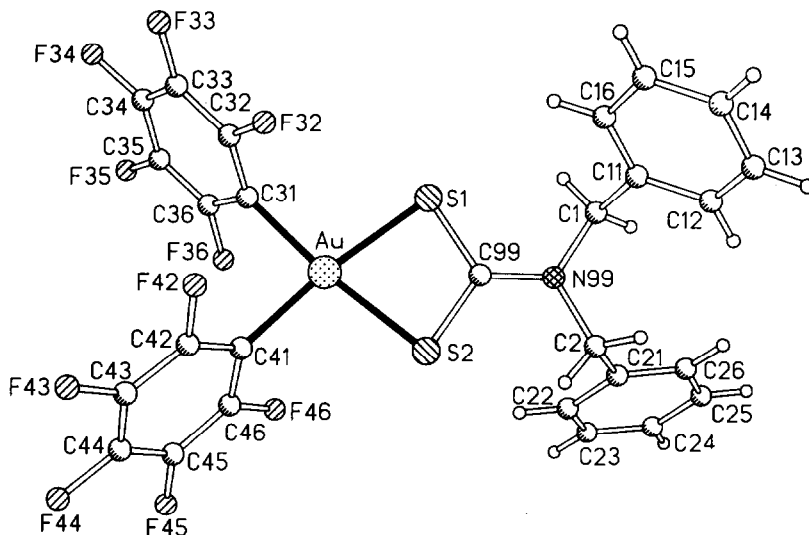


Fig. 1. The molecule of complex X in the crystals, showing the atom numbering scheme. Radii are arbitrary.

crystallographic data are needed before structural trends become clear. In the context of these known structures, the molecular dimensions of complex X are "normal".

Experimental

Instrumentation and general experimental techniques were as described previously [4]. ^1H NMR spectra were recorded on Varian XL200 spectrometer in CDCl_3 ; chemical shifts are quoted relative to SiMe_4 . The yields, melting points, C, H, N and Au analyses, conductivities and molecular weights of the novel complexes are listed in Table 1.

Preparation of the complexes

$Q[\text{Au}(\text{C}_6\text{F}_5)_2(\text{S}_2\text{CNR}_2)]$ ($Q = \text{Bu}_4\text{N}$, $R = \text{Me}$ (I), Et (II) or CH_2Ph (III) or $Q = \text{N}(\text{PPh}_3)_2$, $R = \text{Me}$ (IV)). To an acetone solution (20 ml) of $\text{Au}(\text{C}_6\text{F}_5)_3(\text{tht})$ [2] (0.157 g, 0.2 mmol) was added $\text{Na}(\text{S}_2\text{CNMe}_2) \cdot 2\text{H}_2\text{O}$ (0.036 g, 0.2 mmol), $\text{Na}(\text{S}_2\text{CNEt}_2) \cdot 3\text{H}_2\text{O}$ (0.045 g, 0.2 mmol) or $\text{Na}[\text{S}_2\text{CN}(\text{CH}_2\text{Ph})_2]$ (0.059, 0.2 mmol). The mixture was stirred for 2 h at room temperature then the yellow solution was evaporated to dryness. A dichloromethane solution (20 ml of $[\text{N}(\text{PPh}_3)_2]\text{Cl}$ (0.115 g, 0.2 mmol) or $(\text{Bu}_4\text{N})\text{ClO}_4$ (0.068 g, 0.2 mmol) was added to the residue and the mixture stirred for 1 h at room temperature. The precipitated NaCl or NaClO_4 was filtered off and washed (2×5 ml) with dichloromethane. The combined filtrate and washings were vacuum-evaporated to ca. 5 ml, and upon addition of n-hexane (20 ml) complexes I–IV precipitated out. ^1H NMR of I: δ 3.44(s, N–CH₃), 3.27(m, N–CH₂), 1.68(m, CH₂), 1.45(m, CH₂) and 1.01 ppm (t, C–CH₃, $J(\text{HH})$ 7.2 Hz).

$\text{Bu}_4\text{N}[(\mu\text{-S}_2\text{CNR}_2)\{\text{Au}(\text{C}_6\text{F}_5)_3\}_2]$ ($R = \text{Me}$ (V), Et (VI) or CH_2Ph (VII)). To an acetone solution (20 ml) of $\text{Au}(\text{C}_6\text{F}_5)_3(\text{tht})$ [2] (0.157 g, 0.2 mmol) was added 0.2 mmol of $\text{Na}(\text{S}_2\text{CNR}_2) \cdot n\text{H}_2\text{O}$ ($R = \text{Me}$, Et or CH_2Ph) and the mixture was stirred

Table 1
Analytical data for products

Complex	Yield (%)	Analysis Found (calcd.) (%)				M.p. (°C)	Λ_M^a	Mol. wt. ^b (Found (calcd.))
		C	H	N	Au			
I NBu ₄ [Au(C ₆ F ₅) ₃ (S ₂ CNMe ₂)]	89	41.6 (41.9)	4.0 (4.0)	2.4 (2.65)	18.25 (18.55)	190	108	
II NBu ₄ [Au(C ₆ F ₅) ₃ (S ₂ CNEt ₂)]	60	43.1 (43.0)	4.1 (4.25)	2.45 (2.55)	18.15 (18.1)	186	98	
III NBu ₄ [Au(C ₆ F ₅) ₃ (S ₂ CN(CH ₂ Ph) ₂)]	70	48.4 (48.5)	4.15 (4.15)	2.3 (2.3)	16.0 (16.25)	121	90	
IV N(PPh ₃) ₂ [Au(C ₆ F ₅) ₃ (S ₂ CNMe ₂)]	84	50.45 (50.45)	2.8 (2.65)	2.1 (2.05)	14.6 (14.5)	166	107	
V NBu ₄ [(μ -S ₂ CNMe ₂)(Au(C ₆ F ₅) ₃) ₂]	89	37.9 (37.55)	2.5 (2.4)	1.5 (1.6)	20.7 (20.4)	164	91	
VI NBu ₄ [(μ -S ₂ CNEt ₂)(Au(C ₆ F ₅) ₃) ₂]	84	38.6 (38.3)	2.55 (2.6)	1.55 (1.55)	21.8 (22.05)	203	95	
VII NBu ₄ [(μ -S ₂ CN(CH ₂ Ph) ₂)(Au(C ₆ F ₅) ₃) ₂]	83	42.15 (42.1)	2.7 (2.65)	1.35 (1.45)	20.55 (20.6)	158(d)	92	
VIII Au(C ₆ F ₅) ₂ (S ₂ CNMe ₂)	88	27.4 (27.65)	0.95 (0.9)	2.25 (2.15)	29.85 (30.25)	218	1	690 (651)
IX Au(C ₆ F ₅) ₂ (S ₂ CNEt ₂)	66	30.3 (30.05)	1.45 (1.5)	2.25 (2.05)	28.75 (29.0)	162	2	686 (679)
X Au(C ₆ F ₅) ₂ (S ₂ CN(CH ₂ Ph) ₂)	73	40.0 (40.35)	2.0 (1.75)	1.75 (1.75)	24.2 (24.5)	165	1	811 (803)

^a In acetone, ohm⁻¹ cm² mol⁻¹. ^b In chloroform.

for 2 h at room temperature. The procedure described for complexes I–IV gave the yellow V–VII. ^1H NMR of V: δ 3.57(s, N–CH₃), 3.12(m, N–CH₂), 1.58(m, CH₂), 1.39(m, CH₂) and 0.97 ppm (t, C–CH₃, $J(\text{HH})$ 7.2 Hz).

$\text{Au}(\text{C}_6\text{F}_5)_2(\text{S}_2\text{CNR}_2)$ ($R = \text{Me}$ (VIII), Et (IX) or CH_2Ph (X)). To a dichloromethane solution (20 ml) of $[\text{Au}(\mu\text{-Cl})(\text{C}_6\text{F}_5)_2]_2$ [5] (0.113 g, 0.1 mmol) was added 0.2 mmol of $\text{Na}(\text{S}_2\text{CNR}_2) \cdot n\text{H}_2\text{O}$ ($R = \text{Me}, \text{Et}$ or CH_2Ph). The mixture was stirred for 2 h at room temperature and the precipitated NaCl was then filtered off and washed (2×5 ml) with dichloromethane. The yellow filtrate (combined with the washings) was vacuum evaporated to ca. 5 ml, and upon addition of n-hexane (20 ml) complexes VIII–X precipitated out. ^1H NMR of VIII, δ 3.38(s, CH₃) ppm; IX, δ 3.73(q, CH₂, $J(\text{HH})$ 7.2 Hz) and 1.40(t, CH₃) ppm; X, δ 7.46(m, Ph) and 4.77(s, CH₂) ppm.

Complex IX was also obtained by the following methods: (a) To a dichloromethane solution (20 ml of 0.2 mmol) of $[\text{Au}(\text{C}_6\text{F}_5)_2(\text{tht})_2]\text{ClO}_4$ [6] or $[\text{Au}(\text{C}_6\text{F}_5)_2(\text{PPh}_3)(\text{OCIO}_3)]$ [8] was added $\text{Na}(\text{S}_2\text{CNEt}_2) \cdot 3\text{H}_2\text{O}$ (0.045 g, 0.2 mmol). The mixture was stirred for 2 h at room temperature and the precipitated NaClO_4 was then filtered off and the filtrate was vacuum evaporated to ca. 5 ml. Addition of n-hexane (20 ml) led to precipitation of IX as a pale yellow solid.

(b) To a suspension of $[\text{Au}(\text{S}_2\text{CNEt}_2)]_2$ (0.069 g, 0.1 mmol, obtained from $\text{AuCl}(\text{tht})$ and an equimolar amount of $\text{Na}(\text{S}_2\text{CNEt}_2) \cdot 2\text{H}_2\text{O}$) in dichloromethane (20 ml), was added $\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}$ [8] (0.115 g, 0.2 mmol). The mixture was refluxed for 6 h and the precipitated TlCl was then filtered off and washed (2×5 ml) with dichloromethane. The filtrate (plus washings) was evaporated to ca. 5 ml, and upon addition of n-hexane (20 ml) complex IX precipitated out.

X-Ray structure determination of complex X

It proved difficult to obtain suitable single crystals of the complex; the usual diffusion methods yielded clumps of irregular crystals that were difficult to separate and contained solvent of crystallization, easily lost to the atmosphere. However, when solutions of X in CH_2Cl_2 /petroleum ether were left to stand in stoppered tubes for several weeks, large single crystals of a different modification formed; these contained no solvent and were air-stable.

Crystal data: $\text{C}_{27}\text{H}_{14}\text{AuF}_{10}\text{NS}_2$, M 803.5, monoclinic, $P2_1/c$, a 9.065(3), b 8.021(2), c 36.055(13) Å, β 90.38(3)°, V 2621 Å³, $Z = 4$, D_x 2.03 g cm⁻³, $\mu(\text{Mo-K}_\alpha)$ 5.8 mm⁻¹, $F(000)$ 1536.

Data collection and processing. A pale yellow prism 0.65 \times 0.5 \times 0.5 mm was used to record 6474 profile-fitted intensities [9] on a Stoe–Siemens four-circle diffractometer (Mo–K α radiation, $2\theta_{\text{max}}$ 55°). Of 6008 unique reflections (R_{int} 0.033), 4683 with $F > 4\sigma(F)$ were used for all calculations (program system SHELXTL). Absorption corrections were based on ψ -scans (transmission factors 0.52–0.74). Cell constants were refined from 2θ values of 51 reflections in the range 20–23°.

Structure solution and refinement. The structure was solved by the heavy-atom method and refined anisotropically to $R = 0.046$, $R' = 0.045$. Hydrogen atoms were included in the refinement using a riding model. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0004F^2$. 370 parameters were refined. The maximum residual electron density was ca. 1 e Å⁻³ near the gold atom.

Final atom coordinates are presented in Table 2, with selected bond lengths and

Table 2

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for complex X

	x	y	z	U^a
Au	4000.9(3)	729.1(3)	1247.6(1)	38(1)
S(1)	2914(2)	2814(2)	879(1)	45(1)
S(2)	2020(2)	1713(3)	1600(1)	49(1)
C(99)	1712(8)	3100(8)	1242(2)	40(2)
N(99)	651(6)	4260(7)	1247(2)	44(2)
C(1)	419(8)	5408(8)	934(2)	45(2)
C(2)	-321(8)	4455(9)	1568(2)	47(2)
C(11)	-864(8)	4875(9)	694(2)	44(2)
C(12)	-2316(9)	5351(10)	782(2)	58(3)
C(13)	-3479(10)	4846(11)	570(3)	66(3)
C(14)	-3259(10)	3849(11)	262(3)	69(3)
C(15)	-1844(10)	3372(11)	171(2)	65(3)
C(16)	-664(9)	3872(9)	390(2)	53(3)
C(21)	55(8)	5964(9)	1799(2)	44(2)
C(22)	1272(9)	5929(10)	2038(2)	57(3)
C(23)	1608(9)	7275(12)	2253(2)	64(3)
C(24)	750(9)	8697(11)	2237(2)	59(3)
C(25)	-421(9)	8756(11)	2000(3)	61(3)
C(26)	-778(8)	7396(11)	1778(2)	59(3)
C(31)	5714(7)	145(8)	904(2)	36(2)
C(32)	5500(8)	-655(9)	570(2)	48(2)
C(33)	6657(10)	-1070(10)	341(2)	57(3)
C(34)	8057(9)	-717(10)	449(3)	60(3)
C(35)	8314(8)	27(10)	784(2)	54(3)
C(36)	7170(8)	429(9)	1002(2)	47(2)
F(32)	4119(5)	-1068(6)	459(1)	65(2)
F(33)	6385(6)	-1844(7)	15(1)	80(2)
F(34)	9196(6)	-1164(7)	233(2)	93(2)
F(35)	9721(5)	330(8)	892(2)	92(2)
F(36)	7461(5)	1212(6)	1330(1)	68(2)
C(41)	4713(7)	-1084(8)	1607(2)	38(2)
C(42)	4619(7)	-2750(9)	1520(2)	44(2)
C(43)	5149(8)	-3987(8)	1741(2)	47(3)
C(44)	5766(8)	-3576(9)	2073(2)	46(2)
C(45)	5879(8)	-1946(10)	2181(2)	50(3)
C(46)	5368(8)	-739(9)	1948(2)	45(2)
F(42)	3972(5)	-3204(6)	1190(1)	72(2)
F(43)	5074(7)	-5593(6)	1639(2)	85(2)
F(44)	6346(5)	-4778(7)	2294(1)	77(2)
F(45)	6510(6)	-1542(7)	2505(1)	75(2)
F(46)	5529(6)	875(5)	2050(1)	65(2)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

angles in Table 3. Further details of the structure determination (structure factors, temperature factors, complete bond lengths and angles, H atom coordinates) have been deposited with the Fachinformationszentrum Energie Physik Mathematik, 7514 Eggenstein-Leopoldhafen 2, W. Germany. Any request for this material should quote reference number CSD 52663 and the complete literature citation.

Table 3

Selected bond lengths (Å) and angles (deg.) for complex X

Au-S(1)	2.349(2)	Au-S(2)	2.343(2)
Au-C(31)	2.047(6)	Au-C(41)	2.049(6)
S(1)-C(99)	1.725(7)	S(2)-C(99)	1.724(7)
C(99)-N(99)	1.338(9)	N(99)-C(1)	1.472(9)
N(99)-C(2)	1.468(9)	C(1)-C(11)	1.506(10)
C(2)-C(21)	1.508(10)		
Si(1)-Au-S(2)	75.4(1)	S(1)-Au-C(31)	97.9(2)
S(2)-Au-C(31)	172.8(2)	S(1)-Au-C(41)	172.9(2)
S(2)-Au-C(41)	97.8(2)	C(31)-Au-C(41)	89.0(3)
Au-S(1)-C(99)	85.9(2)	Au-S(2)-C(99)	86.1(2)
S(1)-C(99)-S(2)	112.5(4)	S(1)-C(99)-N(99)	124.0(5)
S(2)-C(99)-N(99)	123.5(5)	C(99)-N(99)-C(1)	121.6(6)
C(99)-N(99)-C(2)	121.3(6)	C(1)-N(99)-C(2)	117.1(5)
N(99)-C(1)-C(11)	111.6(6)	N(99)-C(2)-C(21)	112.8(6)

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