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Bis(3-methyl-1,3-thiazolinylidene)gold(I) Trifluoromethanesulfonate

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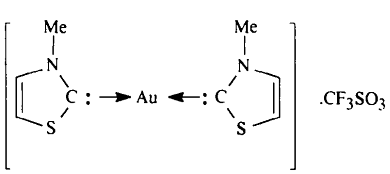
Abstract

The structure of $[Au(C_4H_5NS)_2]CF_3SO_3$ displays essentially linear cationic gold(I) units [C11—Au—C21 175.8 (7)°]. These linear cations are aggregated through alternating Au···Au interactions [3.1926 (11) and 3.4830 (10) Å] to form chains of Au atoms parallel to the *c* axis.

Comment

Recent studies have shown that some gold(I) compounds aggregate through second-order Au···Au bonding to form dimers (Schmidbaur, Weidenhiller, Steigelmann & Mueller, 1990), tetramers (Bates & Waters, 1985) or even polymers (Ahrland, Aurivillius, Dreisch, Noren & Oskarsson, 1992). It is believed that correlation and relativistic effects (Pyykkö & Zhao, 1991) are involved in this novel type of interaction ('aurophilicity').

The structure of chloro(trimethylphosphine)gold(I) (Angermaier, Zeller & Schmidbaur, 1994) shows aggregation of monomeric units to form helical chains, in contrast to the structure of chloro(triethylphosphine)gold(I) (Tiekink, 1989), which shows no significant Au···Au interactions. This confirms that steric hindrance influences secondary Au bonding.



(I)

The structure of (I) shows two planar 3-methylthiazolinylidene ligands [dihedral angle between the planes is 10.0 (3)°] coordinating a gold(I) centre, with the two methyl groups on the same side of the C11—Au—C21 bonds. The Au—C bond lengths [Au—C11 2.01 (2) and Au—C21 2.06 (2) Å] correspond to those found for bis(1,2-dihydropyridylidene)gold(I) trifluoromethanesulfonate dihydrate [2.02 (2) Å; Raubenheimer, Toerien *et al.*, 1994] and (pentafluorobenzene)(3,4-dimethylthiazolinylidene)gold(I) [1.96 (9) Å; Raubenheimer, Scott, Roos & Otte, 1990]. The N—$C_{carbene}$ bond lengths [N1—C11 1.34 (2) and N2—C21 1.28 (3) Å] agree with those found for bis(1-benzylimidazolinylidene)gold(I) chloride [1.33 (1) Å; Bovio, Burini & Pietroni, 1993] and reveal a high degree of multiple-bond character, as analogous C—N distances of 1.31–1.34 Å have been shown to correspond to a bond order of approximately 1.7 (Cotton & Lukehart, 1972).

Two different Au interactions determine the arrangement of the complex molecules in the lattice. The shorter Au···Au interactions [Fig. 1; Au···Au^i 3.1926 (11) Å; symmetry code: (i) $1-x$, y, $\frac{1}{2}-z$] result in the formation of dimeric units, similar to those formed by bis(4-methylthiazolinylidene)gold(I) tetrachlorozincate (Kruger, Olivier, Otte & Raubenheimer, 1996), with the S atoms turned towards each other. This interaction is longer than that found for (4-methylthiazolyl)(4-methylthiazolinylidene)gold(I) (Raubenheimer, Scott *et al.*, 1994), where extensive intermolecular hydrogen bonding enhances the secondary Au bonding. The methyl groups in the dimeric units of (I) are directed away from each other and therefore do not affect the Au···Au interaction in terms of steric hindrance. The resulting C11—Au···Au^i—C11^i dihedral angle of 110.9 (6)° agrees with the findings of Patheneni & De-

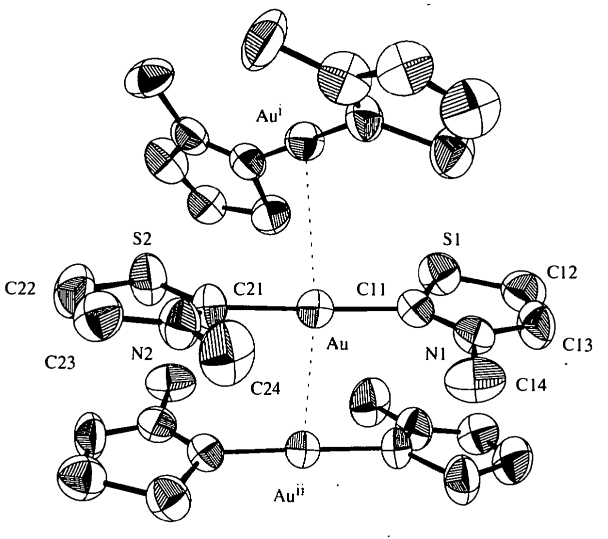


Fig. 1. The two types of interaction in compound (I) which result in the chain structure. Ellipsoids are plotted at the 50% probability level.

siraju (1993) that shorter Au interactions (<3.5 Å) prefer staggered conformations.

The longer Au interactions [Fig. 1; Au$\cdots$Au^{ii} 3.4830 (10) Å; symmetry code: (ii) $1-x$, $1-y$, $1-z$] are exhibited by molecules in the eclipsed conformation across an inversion centre, forcing a dihedral angle of 180°. The two connecting molecules are offset parallel to each other, resulting in infinite zigzag chains. The methyl groups from different cations are on opposite sides of the C11—Au—C12 bonds, facilitating the Au interaction by reduced steric hindrance. The chains form columns of cationic bis(carbene) complexes parallel to the *c* axis, separated by trifluoromethanesulfonate anions.

Experimental

The title compound, (I), was synthesized and isolated according to the method described by Raubenheimer, Scott *et al.* (1994).

Crystal data

$[Au(C_4H_5NS)_2]CF_3SO_3$
$M_r = 544.334$
Orthorhombic
Pbcn
$a = 20.348\ (4)$ Å
$b = 13.501\ (2)$ Å
$c = 11.701\ (3)$ Å
$V = 3215\ (1)$ Å^3
$Z = 8$
$D_x = 2.25$ Mg m^{-3}
D_m not measured

Mo *Kα* radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 2$–$30°$
$\mu = 9.84$ mm^{-1}
$T = 293$ K
Needle
$0.38 \times 0.11 \times 0.04$ mm
Yellow

Data collection

Enraf–Nonius CAD-4*F* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Matthews, 1968)
$T_{min} = 0.602$, $T_{max} = 0.999$
5751 measured reflections
4676 independent reflections

2090 observed reflections [$F > \sigma(F)$]
$R_{int} = 0.154$
$\theta_{max} = 30°$
$h = -1 \rightarrow 28$
$k = -1 \rightarrow 18$
$l = -1 \rightarrow 16$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on *F*
$R = 0.066$
$wR = 0.054$
$S = 2.948$
2090 reflections
185 parameters
H atoms not included in the refinement
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{max} = 0.053$
$\Delta\rho_{max} = 3.393$ e Å^{-3} (0.77 Å from Au)
$\Delta\rho_{min} = -4.857$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Au	0.51578 (3)	0.57682 (5)	0.38364 (5)	0.0570 (4)
S1	0.5943 (3)	0.3814 (4)	0.2879 (4)	0.071 (3)
N1	0.6579 (7)	0.5095 (10)	0.3929 (11)	0.065 (11)
C11	0.5958 (8)	0.4924 (12)	0.3593 (13)	0.060 (10)
C12	0.6772 (9)	0.3545 (15)	0.3002 (16)	0.081 (13)
C13	0.7047 (9)	0.4366 (13)	0.3614 (15)	0.076 (12)
C14	0.6783 (9)	0.6033 (12)	0.4653 (15)	0.082 (13)
S2	0.3607 (2)	0.6376 (4)	0.3700 (5)	0.078 (3)
N2	0.4388 (7)	0.7620 (10)	0.4401 (10)	0.071 (10)
C21	0.4376 (7)	0.6719 (13)	0.4042 (13)	0.061 (11)
C22	0.3285 (8)	0.7536 (14)	0.4081 (15)	0.09 (3)
C23	0.3770 (9)	0.8100 (12)	0.4447 (15)	0.075 (13)
C24	0.5015 (8)	0.8133 (15)	0.4759 (18)	0.098 (24)
S3	0.6696 (3)	0.8980 (4)	0.6359 (7)	0.104 (5)
O1	0.7158 (9)	0.8675 (14)	0.7422 (16)	0.184 (2)
O2	0.6949 (9)	0.9751 (12)	0.5714 (17)	0.197 (25)
O3	0.6507 (9)	0.8070 (11)	0.5810 (15)	0.163 (14)
C3	0.6090 (12)	0.9422 (18)	0.7289 (19)	0.102 (8)
F1	0.5801 (9)	0.8734 (13)	0.7824 (19)	0.191 (21)
F2	0.6255 (9)	1.0185 (15)	0.7847 (13)	0.182 (17)
F3	0.5617 (8)	0.9727 (15)	0.648 (3)	0.33 (3)

Table 2. *Selected geometric parameters (Å, °)*

Au—C11	2.01 (2)	C12—C13	1.43 (3)
Au—C21	2.06 (2)	S2—C21	1.68 (2)
S1—C11	1.72 (2)	S2—C22	1.76 (2)
S1—C12	1.73 (2)	N2—C21	1.28 (3)
N1—C11	1.34 (2)	N2—C23	1.43 (2)
N1—C13	1.42 (2)	N2—C24	1.51 (2)
N1—C14	1.58 (2)	C22—C23	1.31 (3)
Au$\cdots$Au^{i}	3.1926 (11)	Au$\cdots$Au^{ii}	3.4830 (10)
C11—Au—C21	175.8 (7)	N1—C13—C12	114.0 (15)
C11—Au—Au^{i}	91.5 (5)	C21—S2—C22	92.2 (8)
C21—Au—Au^{i}	87.7 (5)	C21—N2—C23	115.6 (13)
C11—S1—C12	97.1 (9)	C21—N2—C24	122.4 (15)
C11—N1—C13	115.6 (13)	C23—N2—C24	122.2 (15)
C11—N1—C14	123.0 (13)	Au—C21—S2	121.2 (9)
C13—N1—C14	121.3 (13)	Au—C21—N2	128.0 (11)
Au—C11—S1	123.2 (9)	S2—C21—N2	110.6 (11)
Au—C11—N1	128.5 (12)	S2—C22—C23	108.8 (15)
S1—C11—N1	108.8 (11)	N2—C23—C22	112.5 (17)
S1—C12—C13	105.1 (13)		
C11—Au$\cdots$Au^{i}—C11^{i}	110.9 (7)		

Symmetry codes: (i) $1-x, y, \frac{1}{2}-z$; (ii) $1-x, 1-y, 1-z$.

Uncertainty in the positions of the atoms in the trifluoromethanesulfonate counterion required the use of bond-length restraints in the refinement of the crystal structure. Ideal values were obtained from a search for ordered trifluoromethanesulfonate ions in the Cambridge Structural Database (Allen *et al.*, 1979). The average values from 131 structures with *R* values less than 0.10 are C—S 1.79, C—F 1.31 and S—O 1.42 Å.

Data collection: Enraf–Nonius CAD-4*F* diffractometer software. Data reduction: *Xtal*3.0 *ADDREF SORTRF* (Hall & Stewart, 1990). Program(s) used to solve structure: *Xtal*3.0 *FOURR*. Program(s) used to refine structure: *Xtal*3.0 *CRYLSQ*. Molecular graphics: *ORTEP* (Johnson, 1965) and *SCHAKAL* (Keller, 1988). Software used to prepare material for publication: *Xtal*3.0 *BONDLA CIFIO*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1002). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Dichlorobis(1-methylcytosine)copper(II)

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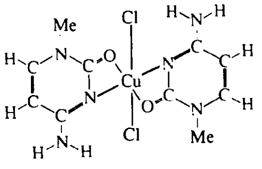
Abstract

The structure of bis[4-amino-1-methyl-2(1*H*)-pyrimidinone]dichlorocopper(II) consists of discrete $[CuCl_2(C_5H_7N_3O)_2]$ units. The coordination about the Cu^{II} ion is distorted 4 + 2 octahedral. The non-equivalent 1-methylcytosine ligands are bonded to the metal through N(3) and more weakly through O(2). The average N—Cu—Cl *trans* angle is 159.9 (1)°.

Comment

The compound bis(1-methylcytosinium) tetrachlorocuprate(II) has been described previously (Valle, Ettorre & Peruzzo, 1995). The structure of the title compound, (I), consists of discrete $[CuCl_2(C_5H_7N_3O)_2]$ units containing non-equivalent 1-methylcytosine and chloride ligands. The coordination about the Cu^{II} ion is distorted 4 + 2 octahedral. The Cu—N(3), Cu—N(3′), Cu—Cl(1) and Cu—Cl(2) bonds are normal. The difference in the length between the Cu—Cl(1) and Cu—Cl(2) bonds may be accounted for by the difference in the geometry between the Cl(1)···N(4)(x, $1 - y$, $z + \frac{1}{2}$) and Cl(2)···N(4)(x, $1 - y$, $z + \frac{1}{2}$) hydrogen bonds.



(I)

The Cu—O(2) and Cu—O(2′) contacts can be considered as weak bonds, which result in the Cu—N(3)—C(4) and Cu—N(3′)—C(4′) angles being larger than the Cu—N(3)—C(2) and Cu—N(3′)—C(2′) angles. There is an intramolecular hydrogen bond between N(4′) and O(2). Each molecule is linked to four neighbouring units by hydrogen bonds through its N(4), N(4′), O(2′), Cl(1) and Cl(2) atoms. In the related complex $[CuCl_2(C_4H_5N_3O)_2]$, (II), cytosine ligands are also co-

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† Deceased.