Acta Cryst. (1995). C**51**, 1814–1816

(1,3-Dimethylimidazolinylidene)(1-methylimidazolinylidene)gold(I) Trifluoromethanesulfonate

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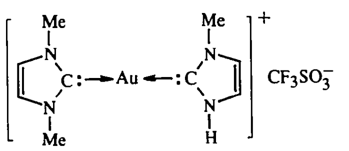
(*Received* 14 *October* 1994; *accepted* 3 *March* 1995)

Abstract

The crystal structure of the title compound consists of cationic $[Au(C_4H_6N_2)(C_5H_8N_2)]^+$ units with $CF_3SO_3^-$ counterions. Each Au^I centre approaches linear coordination with the two differing imidazolinylidene ligands [C—Au—C 179.0 (6)°]. These two essentially planar ligands are almost coplanar having a dihedral angle of 2.54 (4)° between their planes.

Comment

The reaction of 1-alkyl-2-lithioimidazolyl with $[AuCl(L)]$ (L = Me_2S or PPh_3) leads to the formation of oligomeric, possibly trimeric, gold(I) compounds (Bonati, Burini & Pietroni, 1989). The analogous reaction of 2-lithio-4-methylthiazolyl with $[AuCl(PPh_3)]$ and subsequent protonation leads to the formation of 4-methylthiazolinylidene(triphenylphosphine)gold(I) trifluoromethanesulfonate (Raubenheimer *et al.*, 1994), as well as the above mentioned polymers. However, reaction of two molar amounts of 2-lithio-methylimidazolyl with one molar amount of [AuCl(tht)] (tht = tetrahydrothiophene) produced a bis(methylimidazolyl)aurate. Subsequent alkylation, followed by protonation, produced a unique mixed biscarbene complex of gold(I), (I). Attempts to synthesize similar thiazole complexes proved unsuccessful as homoleptic rearrangement occurred as described by Raubenheimer *et al.* (1994).



(I)

The crystal structure of the title compound contains stacks of cations parallel to the *a* axis. The individual units stack with parallel molecular planes normal to the stacking direction and are offset such that an Au···Au—C11 angle of 59.6 (4)° results. The Au—$C_{carbene}$ bond lengths of 1.99 (2) Å are similar to those found for (1-benzyl-3-benzoylimidazolinylidene)chlorogold(I) [1.97 (1) Å; Bovio, Burini & Pietroni, 1993] and (1-benzyl-3-ethoxycarbonylimidazolinylidene)chlorogold(I) [1.97 (8) Å; Bonati, Burini, Pietroni & Bovio, 1991], indicating that the ligand *trans* to the carbene C atom, when changing from Cl to 1,3-dimethylimidazolinylidene, has little influence on the Au—$C_{carbene}$ bond length. The Au—$C_{carbene}$ bond length of (I) also corresponds to that found for 3,4-dimethylthiazolinylidene(pentafluorobenzene)gold(I) [1.96 (9) Å; Raubenheimer, Scott, Roos & Otte, 1990], which indicates that the gold–carbene bond length is probably determined by the metal and not by the ligand (Cotton & Lukehart, 1972). The substituents on the N atoms in the title compound also have no apparent influence on the N—$C_{carbene}$ bond lengths.

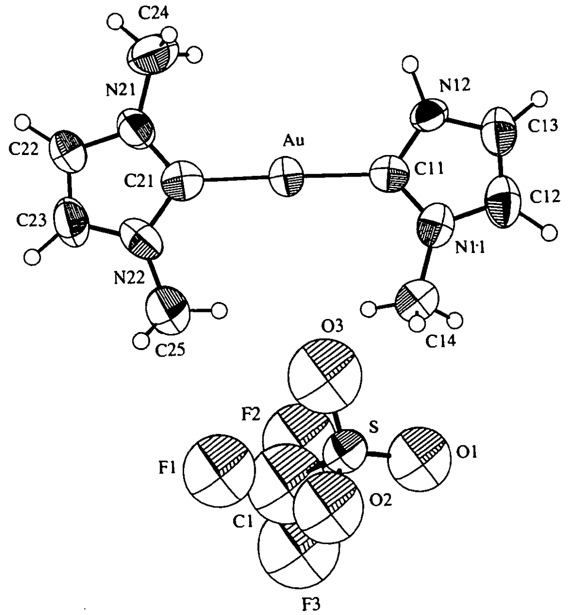


Fig. 1. *ORTEP* (Johnson, 1965) drawing of (I) showing the atomic labelling scheme and displacement ellipsoids drawn at the 50% probability level.

Experimental

Reactions and manipulations were carried out under argon using standard Schlenk techniques. Solvents were dried and freshly distilled under nitrogen before use. [AuCl(tht)] was prepared according to a literature method (Uson & Laguna, 1986). Methylimidazole was purchased from Fluka, methyltrifluoromethanesulfonate and trifluoromethanesulfonic acid from Aldrich and butyllithium from Merck. A tetrahydrofuran solution (30 ml) of methylimidazole (0.18 g, 2.6 mmol) was cooled to 233 K and treated with butyllithium (1.8 ml, 1.6*M*, 2.8 mmol). The resulting yellow mixture was stirred for 30 min before cooling to 195 K. [AuCl(tht)] (0.35 g, 1.0 mmol) was added and the solution stirred for another 2 h. After alkylation with CF_3SO_3Me (0.12 ml, 1.08 mmol), the temperature was allowed to rise to room temperature. The solution was again cooled to 195 K and treated with CF_3SO_3H (0.096 ml, 1.08 mmol) before the temperature was increased to 293 K over a period of 1 h. The solvent was removed under vacuum and the white residue washed with *n*-pentane (2 × 20 ml) and diethyl ether (2 × 20 ml), before dissolution in CH_2Cl_2 (30 ml) and filtration through anhydrous $MgSO_4$. Colourless needle-shaped crystals formed overnight after addition of *n*-pentane (5 ml) and cooling to 293 K.

Crystal data

$[Au(C_4H_6N_2)(C_5H_8N_2)]$-$CF_3SO_3$
$M_r = 524.3$
Monoclinic
$P2_1/n$
$a = 6.799\ (2)$ Å
$b = 10.400\ (2)$ Å
$c = 22.909\ (5)$ Å
$\beta = 96.86\ (2)°$
$V = 1608.3\ (6)$ Å^3
$Z = 4$
$D_x = 2.165$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 1\text{–}15°$
$\mu = 9.86$ mm^{-1}
$T = 293$ K
Needle
0.27 × 0.08 × 0.06 mm
Colourless

Data collection

Enraf–Nonius CAD-4*F* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1983)
$T_{min} = 0.880$, $T_{max} = 0.998$
3516 measured reflections
2909 independent reflections

2088 observed reflections $[F > 2\sigma(F)]$
$R_{int} = 0.088$
$\theta_{max} = 25.23°$
$h = -8 \rightarrow 8$
$k = -1 \rightarrow 12$
$l = -1 \rightarrow 27$
3 standard reflections
frequency: 60 min
intensity decay: 13.3%

Refinement

Refinement on *F*
$R = 0.057$
$wR = 0.04$
$S = 2.045$
2088 reflections
164 parameters
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{max} = 0.073$

$\Delta\rho_{max} = 1.867$ e Å^{-3} (0.76 Å from Au)
$\Delta\rho_{min} = -1.715$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B, 2.3.1)

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

U_{iso} for O, F and C1; $U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for others.

	x	y	z	U_{eq}/U_{iso}
Au	0.24742 (7)	0.54356 (6)	0.46626 (2)	0.0513 (3)
C11	0.257 (2)	0.433 (1)	0.5372 (6)	0.051 (8)
N11	0.242 (2)	0.307 (1)	0.5420 (6)	0.060 (7)
N12	0.278 (1)	0.475 (1)	0.5940 (5)	0.050 (6)
C14	0.208 (3)	0.219 (2)	0.4908 (7)	0.09 (1)
C12	0.253 (2)	0.267 (2)	0.5990 (7)	0.08 (1)
C13	0.279 (2)	0.373 (2)	0.6322 (6)	0.07 (1)
C21	0.235 (2)	0.653 (2)	0.3942 (7)	0.058 (9)
N21	0.246 (2)	0.780 (1)	0.3899 (5)	0.062 (8)
N22	0.217 (2)	0.613 (2)	0.3371 (5)	0.068 (8)
C24	0.262 (2)	0.868 (2)	0.4395 (7)	0.09 (1)
C25	0.200 (3)	0.480 (2)	0.3186 (7)	0.10 (1)
C22	0.237 (2)	0.821 (2)	0.3328 (7)	0.07 (1)
C23	0.217 (2)	0.715 (2)	0.2991 (6)	0.08 (1)
S	−0.3561 (7)	0.1437 (5)	0.3702 (2)	0.080 (3)
O1	−0.287 (2)	0.049 (1)	0.4123 (6)	0.134 (5)
O2	−0.530 (2)	0.107 (2)	0.3361 (6)	0.152 (5)
O3	−0.344 (2)	0.266 (2)	0.3928 (7)	0.177 (7)
C1	−0.159 (5)	0.134 (3)	0.315 (1)	0.22 (2)
F1	−0.219 (2)	0.229 (2)	0.2801 (6)	0.176 (5)
F2	−0.006 (2)	0.164 (2)	0.3427 (7)	0.195 (6)
F3	−0.177 (3)	0.034 (2)	0.2931 (8)	0.233 (8)

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

Au—C11	1.99 (1)	N21—C22	1.37 (2)
Au—C21	2.00 (2)	N22—C25	1.45 (3)
C11—N11	1.32 (2)	N22—C23	1.37 (2)
C11—N12	1.36 (2)	C22—C23	1.34 (2)
N11—C14	1.48 (2)	S—O1	1.42 (1)
N11—C12	1.36 (2)	S—O2	1.39 (1)
N12—C13	1.37 (2)	S—O3	1.37 (2)
C12—C13	1.34 (2)	S—C1	1.95 (3)
C21—N21	1.33 (2)	C1—F1	1.31 (4)
C21—N22	1.36 (2)	C1—F2	1.19 (3)
N21—C24	1.45 (2)	C1—F3	1.15 (4)
C11—Au—C21	179.0 (6)	C21—N22—C23	112 (1)
Au—C11—N11	130 (1)	C23—N22—C25	123 (1)
Au—C11—N12	125.8 (9)	N21—C22—C23	106 (1)
Au—C21—N21	129 (1)	N22—C23—C22	106 (1)
Au—C21—N22	127 (1)	O1—S—O2	112.6 (9)
N11—C11—N12	104 (1)	O1—S—O3	113.0 (9)
C11—N11—C14	123 (1)	O1—S—C1	102 (1)
C11—N11—C12	113 (1)	O2—S—O3	118 (1)
C12—N11—C14	123 (1)	O2—S—C1	103 (1)
C11—N12—C13	111 (1)	O3—S—C1	106 (1)
N11—C12—C13	106 (1)	S—C1—F1	100 (2)
N12—C13—C12	106 (1)	S—C1—F2	106 (2)
N21—C21—N22	103 (1)	S—C1—F3	107 (2)
C21—N21—C24	125 (1)	F1—C1—F2	108 (3)
C21—N21—C22	113 (1)	F1—C1—F3	113 (3)
C24—N21—C22	122 (1)	F2—C1—F3	121 (3)
C21—N22—C25	124 (1)		

Uncertainty in the positions of the atoms of the trifluoromethanesulfonate counterion required the use of bond-length restraints for this ion 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 (5), C—F 1.31 (5) and S—O 1.42 (5) Å. For the H atoms, ideal positions were calculated to fit the maxima of the $\Delta\rho$ map and their parameters were not refined.

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) in *Xtal*3.0 (Hall & Stewart, 1990). 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, along with a packing diagram, have been deposited with the IUCr (Reference: AB1233). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 1816–1819

Potassium Salt of a Synthetic Carboxylic Ionophore

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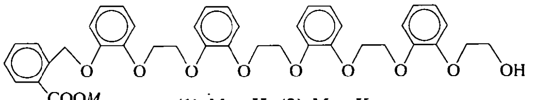
(*Received* 4 *November* 1994; *accepted* 6 *March* 1995)

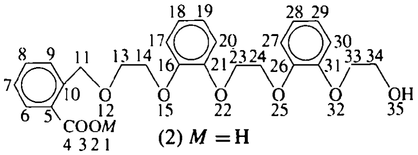
Abstract

The potassium salt of an ω-hydroxycarboxylic acid with five ethereal O atoms, dipotassium bis(2-{[2-(2-{2-[2-(2-hydroxyethoxy)phenoxy]ethoxy}phenoxy)ethoxy]-methyl}benzoate) tetrahydrate, $2K^+.2C_{26}H_{27}O_8^-.4H_2O$, forms a dimeric structure with twofold symmetry, containing two polyether chains and water molecules. The water molecule lying on the twofold axis forms a bridge between the two polyether complexes by coordination to two K^+ ions. The distance between the K^+ ions is 4.231 (3) Å. Each polyether chain wraps around one cation, taking an 'S'-like conformation. The K^+ ion is ninefold coordinated by six ethereal O atoms, including one from another ether chain of the dimer, one hydroxyl group and two water molecules, one of which lies on the twofold axis. O atoms of carboxylato groups do not participate in coordination.

Comment

Naturally occurring carboxylic ionophores such as nigericin, which contain a terminal carboxylic group and one or two hydroxyl groups at the other end, connected with tetrahydrofuran and tetrahydropyran rings, mediate active ion transport across biological and artificial membranes (Pressman, 1976). To understand the complexation properties of ion carriers and how these acyclic compounds utilize conformation for optimum complexation with a guest cation, the crystal structures of various complexes have been determined using X-rays (Duesler & Paul, 1983, and references therein). We have synthesized a series of ω-hydroxycarboxylic acids as model compounds for the natural ionophores to investigate the relationship between the primary molecular structures and transport properties (Kuboniwa *et al.*, 1985; Kuboniwa, Yamaguchi, Nakahama, Hirao & Yamazaki, 1982; Yamaguchi *et al.*, 1988, 1989; Yamazaki, Hirao & Nakahama, 1979; Yamazaki, Nakahama, Hirao & Negi, 1978). Among the compounds, (1) and (2), which have eight and five ethereal O atoms, respectively, show relatively high K^+-ion selectivity. The longer ionophore, (1), exhibits higher transport ability and selectivity than the shorter one, and the crystal structure of the potassium salt of (1), (3), has been reported previously (Kuboniwa, Yamaguchi, Nakahama, Hori & Ohashi, 1988; Kasuga, Nakahama, Yamaguchi, Ohashi & Hori, 1991). The backbone of (3) forms a pseudocyclic ring by head-to-tail hydrogen bonding between the terminal carboxylato and hydroxyl groups and wraps around the cation like the seam of a tennis ball to give a complex with a lipophilic exterior. Although several crystallographic studies on similar synthetic polyethers have been reported (Chacko & Saenger, 1981; Hughes & Wingfield, 1978; Hughes, Mortimer, Parsons, Truter & Wingfield, 1977; Saenger & Reddy, 1979; Saenger & Brand, 1979; Weber & Saenger, 1979*a*,*b*, 1980; Weber, Saenger, Vögtle & Sieger, 1979), little is known about the complexation properties compared with those of the cyclic compounds (Truter, 1973).


(1) M = H, (3) M = K


(2) M = H

Acta Crystallographica Section C
ISSN 0108-2701 ©1995