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Bis[bis(4-methylthiazolin-2-ylidene)gold(I)] Tetrachlorozincate Dichloromethane

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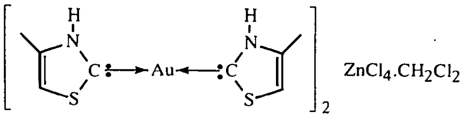
Abstract

The Au centres in the crystal structure of $[Au(C_4H_5NS)_2][ZnCl_4]_{0.5}.0.5CH_2Cl_2$ approach linear coordination [C—Au—C bond angle 179 (1)°]. Monomeric cations connecting through Au···Au interactions [3.330 (2) Å] form dimeric units that link through hydrogen bonds to the tetrachlorozincate anions. Dichloromethane is present as non-bonded and disordered solvent of crystallization.

Comment

The tendency of gold to form aurate complexes upon reaction with 2-lithiothiazolyl reagents has recently been investigated by Raubenheimer *et al.* (1994). The above-mentioned aurate complexes were shown to form mono- and biscarbene complexes after electrophilic attack with H^+ or CH_3^+. Structural information on this type of complex is important to the understanding of contributing resonance structures, as few gold(I) complexes of this type are known. An interesting feature of these, mostly linear, complexes is the Au···Au interaction to form dimeric units in the solid state.

The Au—$C_{carbene}$ bonds [Au—C1 1.92 (2), Au—C5 1.92 (2) Å] of the title compound, (I), are not significantly shorter than equivalent bonds found for *trans*,*trans*-bis[bis(*p*-tolylamino)carbene]gold(I) tetrafluoroborate (2.02 Å; Banditelli, Bonati, Calogero & Valle, 1984) and bis(4,5-dimethylimidazolinylidene)gold(I) chloromonohydrate (2.01 Å; Britten, Lock & Wang, 1992). Moreover, relaxation of the bond-length restraints placed on the ring atoms has the effect of lengthening these bonds slightly.



(I)

The crystal structure of the title compound consists of discrete dimeric bis(4-methylthiazolinylidene)gold(I) cations and tetrachlorozincate anions, bridged through hydrogen bonds (involving N and Cl atoms; Fig. 1) Each Au atom is linearly coordinated by two coplanar 4-methylthiazolin-2-ylidene ligands [C1—Au—C5 179 (1)°]. The ligands are oriented in such a way that the N atoms are on the same side of the cation and are directed towards two of the Cl atoms of the $ZnCl_4$ anion, forming hydrogen bonds [N1···Cl1 3.15 (3), N2···Cl2 3.06 (3) Å; Fig. 2]. The remaining two Cl atoms of the counterion bond to the next cationic Au unit (related by a twofold axis).

Pairs of Au atoms connect through short interactions [3.330 (2) Å] to form dimeric units in a staggered conformation [C1—Au···Au^{i}—C1^{i} torsion angle of 104.0 (10)°] with the S atoms slightly turned towards each other (Fig. 1). This intermolecular bonding pattern results in infinite columns of connected ions parallel to the *c* axis, surrounded by non-bonded disordered dichloromethane.

Pathaneni & Desiraju (1993) reported that in *X*Au*Y* (*X*, *Y* = any element) systems with Au···Au interactions,

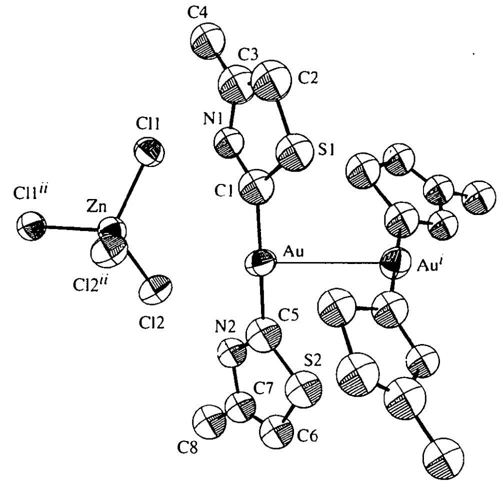


Fig. 1. An *ORTEP* (Hall & Stewart, 1990) drawing of the title compound showing the atomic labelling scheme with displacement ellipsoids drawn at 50% probability.

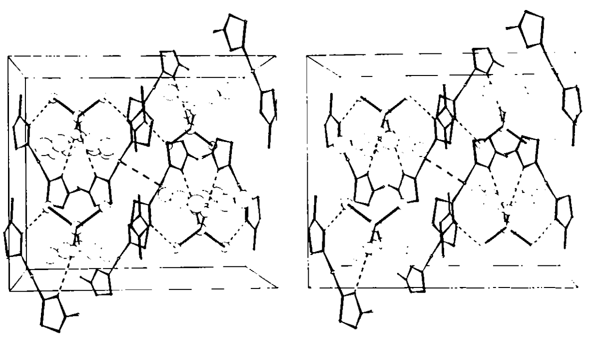


Fig. 2. Packing diagram (*SCHAKAL*; Keller, 1988) (*c* axis horizontal, *b* axis vertical) illustrating the infinite chains along the *c* axis and the atoms approximating the disordered CH_2Cl_2. The radii of the different groups of atoms have been modified to improve the clarity of the illustration.

angular specificity is maintained (*X*—Au···Au—*X* torsion angle 90 or 180/0°), with staggered conformations preferred for shorter Au···Au interactions (< 3.55 Å) and eclipsed conformations for larger Au···Au interactions (> 3.55 Å), the only exceptions being $[Au(PEt_3)Cl]$ (P—Au···Au—P torsion angle 60, 120°; Tiekink, 1989) and $[Au(PMe_3)Cl]$ (P—Au···Au—P torsion angles 143.3, 141.7, 137.6°; Angermaier, Zeller & Schmidbaur, 1994). The angle and Au···Au distance reported here do not correspond with these observations. Investigations are underway to determine the relative contributions of crystal packing and Au interactions to the molecular conformation.

Experimental

Reactions and manipulations were carried out under nitrogen using standard Schlenk techniques. Solvents were dried and freshly distilled under nitrogen before use. [Au(Cl)tht] (Uson & Laguna, 1986) and K_2ZnCl_4 (Mori, Saito & Watanabe, 1961) were prepared according to the methods described in the literature. 4-Methylthiazole was purchased from Fluka and butyllithium from Merck. A thf (tetrahydrofuran) solution (30 cm^3) of 4-methylthiazole (0.40 g, 4.0 mmol) was cooled to 198 K and treated with butyllithium (2.5 cm^3, 1.6 *M*, 4.0 mmol). The resulting yellow mixture was stirred for 45 min before [Au(Cl)thf] (0.64 g, 2.0 mmol) was added and the solution stirred for another 2 h. Dropwise addition of HCl, dissolved in diethyl ether (2.5 cm^3, 0.80 *M*, 2.0 mmol), afforded a light-yellow solution which was stirred for 1 h before addition of K_2ZnCl_4 (0.29 g, 1.0 mmol). The solution was stirred for 1 h before the solvent was removed under vacuum, the residue redissolved in CH_2Cl_2 (30 cm^3) and filtered through anhydrous $MgSO_4$. Yellow orthorhombic prisms crystallized at 293 K.

Crystal data

$[Au(C_4H_5NS)_2][ZnCl_4]_{0.5}$.-
0.5CH_2Cl_2
$M_r = 541.34$
Orthorhombic
$C222_1$
$a = 12.464(3)$ Å
$b = 14.934(3)$ Å
$c = 17.460(3)$ Å
$V = 3250(1)$ Å^3
$Z = 8$
$D_x = 2.21$ Mg m^{-3}

Mo *K*α radiation
$\lambda = 0.7107$ Å
Cell parameters from 25
reflections
$\theta = 10.1$–$15.7°$
$\mu = 10.49$ mm^{-1}
$T = 293$ K
Orthorhombic prism
0.15 × 0.10 × 0.08 mm
Light yellow

Data collection

Enraf–Nonius CAD-4F
diffractometer
ω/2θ scans
Absorption correction:
analytical
$T_{min} = 0.316$, $T_{max} =$
0.419
2492 measured reflections
1282 independent reflections
1744 observed reflections
$[F > 5\sigma(F)]$

$R_{int} = 0.037$
$\theta_{max} = 22.97°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 19$
3 standard reflections
frequency: 60 min
intensity decay: 7.6%

Refinement

Refinement on *F*
$R = 0.050$
$wR = 0.054$
$S = 4.045$
959 reflections
90 parameters
H-atom parameters not
refined
Weighting scheme based
on measured e.s.d.'s

$(\Delta/\sigma)_{max} = 0.031$
$\Delta\rho_{max} = 1.532$ e Å^{-3}
$\Delta\rho_{min} = -1.393$ e Å^{-3}
Extinction correction: none
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 isotropic or 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_{iso}/U_{eq}
Au	0.5722 (1)	0.44195 (9)	0.41858 (9)	0.0599 (8)
Zn	1/2	0.2306 (3)	1/4	0.053 (3)
Cl1	0.5138 (9)	0.1416 (5)	0.3547 (5)	0.064 (6)
Cl2	0.3495 (7)	0.3179 (5)	0.2580 (7)	0.072 (6)
S1	0.7713 (9)	0.3742 (7)	0.5272 (6)	0.078 (3)†
S2	0.4722 (8)	0.6424 (7)	0.3828 (6)	0.086 (3)†
N1	0.659 (2)	0.261 (2)	0.462 (1)	0.058 (8)†
N2	0.398 (2)	0.507 (2)	0.317 (1)	0.060 (8)†
C1	0.667 (2)	0.356 (2)	0.464 (1)	0.08 (1)†
C2	0.804 (3)	0.262 (1)	0.547 (2)	0.09 (1)†
C3	0.736 (2)	0.210 (2)	0.509 (2)	0.09 (1)†
C4	0.721 (3)	0.108 (2)	0.505 (2)	0.08 (1)†
C5	0.479 (2)	0.528 (1)	0.372 (1)	0.08 (1)†
C6	0.369 (2)	0.661 (2)	0.318 (1)	0.08 (1)†
C7	0.335 (2)	0.584 (2)	0.288 (1)	0.07 (1)†
C8	0.247 (2)	0.559 (3)	0.231 (2)	0.09 (1)†
C9‡	1.044 (3)	0.371 (3)	0.296 (2)	0.09 (1)†
C10‡	0.973 (4)	0.378 (3)	0.342 (3)	0.13 (2)†

† U_{iso}. ‡ Disordered solvent sites (see below).

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

Au—C1	1.92 (2)	N2—C7	1.48 (3)
Au—C5	1.92 (2)	C2—C3	1.33 (4)
Au···Au'	3.330 (2)	C3—C4	1.53 (4)
S1—C1	1.73 (3)	C6—C7	1.33 (4)
S1—C2	1.76 (2)	C7—C8	1.53 (4)
S2—C5	1.72 (2)	Zn—Cl1^{ii}	2.266 (9)
S2—C6	1.74 (3)	Zn—Cl1	2.266 (9)
N1—C1	1.42 (4)	Zn—Cl2^{ii}	2.289 (9)
N1—C3	1.48 (4)	Zn—Cl2	2.289 (9)
N2—C5	1.42 (3)	C9—C10	1.21 (7)

C1—Au—C5	179 (1)	N2—C5—Au	124 (2)
C1—S1—C2	98 (1)	S2—C5—Au	130 (1)
C5—S2—C6	97 (1)	C7—C6—S2	111 (2)
C1—N1—C3	117 (2)	C6—C7—N2	112 (2)
C5—N2—C7	115 (2)	C6—C7—C8	134 (3)
N1—C1—S1	103 (2)	N2—C7—C8	114 (2)
N1—C1—Au	128 (2)	Cl1"—Zn—Cl1	108.2 (3)
S1—C1—Au	128 (2)	Cl1"—Zn—Cl2"	110.3 (4)
C3—C2—S1	108 (2)	Cl1"—Zn—Cl2	108.7 (4)
C2—C3—N1	113 (2)	Cl1—Zn—Cl2"	108.7 (4)
C2—C3—C4	133 (3)	Cl1—Zn—Cl2	110.3 (4)
N1—C3—C4	114 (2)	Cl2"—Zn—Cl2	110.6 (3)
N2—C5—S2	106 (2)		

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

The measured data set contained more than the unique set of reflections, including 306 Friedel pairs, allowing the eventual determination of the absolute configuration of the structure (*CRYLSQ*; Hall & Stewart, 1990). The substandard quality of the only available crystals suitable for structure determination required the use of restraints during refinement. After refinement with bond length and dihedral angle restraints [from 12 known structures from the Cambridge Structural Database (Allen *et al.*, 1979)] on the planar rings, difference maps showed two residual peaks with peak heights equivalent to C atoms. These peaks could be interpreted as the manifestation of a CH_2Cl_2 solvent molecule disordered across a twofold axis and were included in the model as C9 and C10, which were considered equivalent to Cl atoms at half weight. Non-restrained refinement of the light atoms (N, C, O, S) with a restricted set of reflection data (maximum $\sin\theta/\lambda$ = 0.30) gave a better set of bonding parameters for the ring atoms. These parameters were used in subsequent restrained refinements with the full set of data. A final difference map was clean with no significant residual electron density peaks. Only the Au, Zn and Cl atoms were refined anisotropically as changes from isotropy for the lighter atoms did not result in improved agreement parameters. No H atoms were located and the low precision achieved did not warrant their inclusion in calculated positions.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Data reduction: *ADDREF*, *ABSORB* and *SORTRF* in *Xtal*3.0 (Hall & Stewart, 1990). Program(s) used to solve structure: *FOURR* in *Xtal*3.0. Program(s) used to refine structure: *CRYLSQ* in *Xtal*3.0. Molecular graphics: *ORTEP* (Johnson, 1965) in *Xtal*3.0; *SCHAKAL* (Keller, 1988). Software used to prepare material for publication: *BONDLA* and *CIFIO* in *Xtal*3.0.

Lists of structure factors, anisotropic displacement parameters, and complete geometry, including contact distances, have been deposited with the IUCr (Reference: KH1025). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Chloro(ethanedithioamide-*S*)bis(triphenylphosphine)silver(I)

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Abstract

The structure of the title compound, $[AgCl(C_2H_4N_2S_2)(C_{18}H_{15}P)_2]$, is reported. Dithiooxamide acts as a monodentate ligand coordinating *via* one S atom to Ag. The coordination polyhedron of the Ag atom is a distorted tetrahedron, with an Ag—S distance of 2.604 (1) Å and an Ag—Cl distance of 2.580 (1) Å.

Comment

Recent studies in our laboratory on copper(I) and silver(I) complexes and cluster compounds reveal that some substances, such as $MO_nS_{4-n}^{2-}$ (M = Mo, W), containing polydentate ligands exhibit strong non-linear optical properties. The examples are $MS_3OCu_2(PPh_3)_3$ (M = Mo,W) (Shi, Hou & Xin, 1995) and $Mo_2S_8Ag_4(PPh_3)_4$ (Ji *et al.*, 1995). An attempt to imitate the $MO_nS_{4-n}^{2-}$ (M = Mo, W) structure with ethanedithioamide did not result in a polynuclear complex but