Di-*μ*-chlorido-bis[bis(tetrahydrothiophene-*κS*)-silver(I)]

Phil Liebing*

Department of Chemistry and Applied Biosciences, Swiss Federal Institute of Technology, Vladimir-Prelog-Weg 2, CH-8093 Zurich, Switzerland. *Correspondence e-mail: liebing@inorg.chem.ethz.ch

The title compound, $[Ag_2Cl_2(C_4H_8S_2)_4]$ or $[Ag_2(\mu\text{-Cl})_2(THT)_4]$ (THT = tetrahydrothiophene), is readily available by reaction of AgCl with THT. In this markedly labile complex, the Ag atoms are coordinated in a distorted tedrahedral fashion by two *μ*-bridging chloride ligands and each two terminal THT ligands. The structure is therefore more similar to that of THT-complexed CuCl than to that of THT-complexed AuCl, and resembles those of other $[Ag_2(\mu\text{-Cl})_2L_4]$-type complexes. The molecule is located on a crystallographic center of inversion.

3D view

Chemical scheme
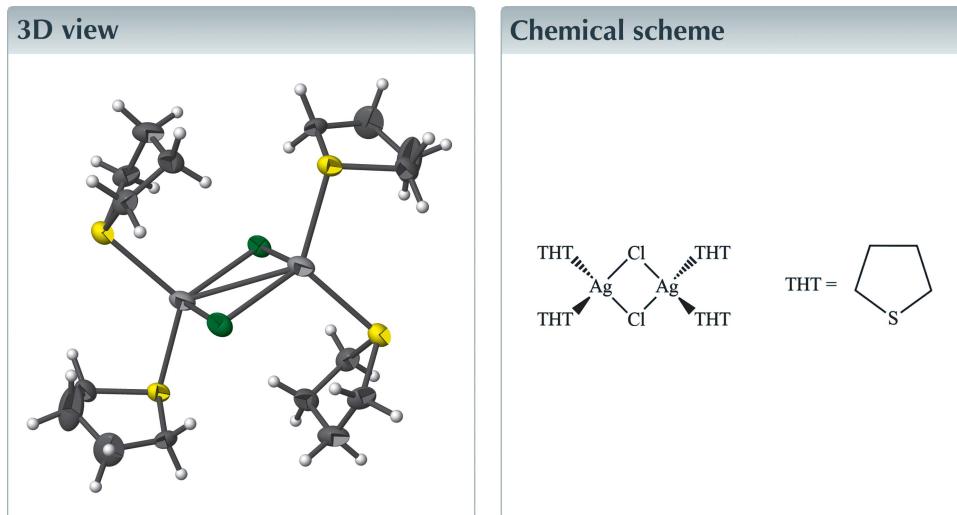
Structure description

In the title compound (Fig. 1), two equivalents of AgCl build a centrosymmetric planar Ag_2Cl_2 ring with *μ*-bridging chloride ligands. The Ag—Cl distances are significantly different at 2.558 (2) and 2.748 (2) Å. Therefore the complex is structurally closely related to a series of other $[Ag_2(\mu\text{-Cl})_2L_4]$-type complexes, *e.g.* with *L* = PPh$_3$ [Ag—Cl = 2.596 (2) and 2.741 (2) Å; Cassel, 1979] and *L* = AsPh$_3$ [Ag—Cl = 2.568 (2) and 2.670 (2) Å; Bowmaker *et al.*, 1997].

Probably as a result of the low bulkiness of the THT ligands, the Ag_2Cl_2 core in the title compound is stretched along the Cl—Cl vector [Cl—Ag—Cl = 100.65 (5)°] while it is slightly stretched along the Ag—Ag vector in the PPh$_3$ complex [Cl—Ag—Cl = 88.03 (6)°]. The shape of the M_2Cl_2 ring in the title compound is therefore similar to those in the polymeric copper(I) complexes $[Cu_2(\mu\text{-Cl})_2(\mu\text{-THT})(THT)_2]$, $[Cu_2(\mu\text{-Cl})_2(\mu\text{-THT})_2]$ and $[Cu_3(\mu\text{-Cl})_3(\mu\text{-THT})_2]$ [Cl—Cu—Cl = 96.8 (1)–105.9 (1)°; Maelger *et al.*, 1992; Solari *et al.*, 1996]. The related gold(I) complex [AuCl(THT)] features a linearly coordinated metal atom and bears no structural resemblance to the title compound (Ahrland *et al.*, 1993).
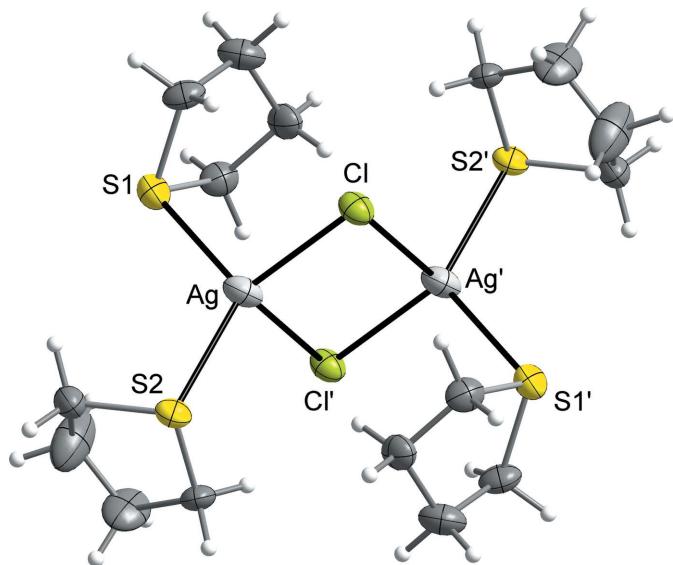
Figure 1
The molecular structure of the title compound in the crystal. Displacement ellipsoids of the non-H atoms are drawn at the 50% probability level and H atoms are drawn as spheres of arbitrary size. [Symmetry code: (') $1 - x, 1 - y, -z$.]

With each two terminal THT ligands, a distorted-tetrahedral coordination of the Ag atoms is realised [Ag—S = 2.623 (2) and 2.554 (2) Å; Cl—Ag—S = 98.94 (7)–123.95 (7)°], where the deformation is stronger than in the related PPh$_3$ complex [Cl—Ag—P = 103.59 (7)–113.92 (7)°; Cassel, 1979]. The angle between the Ag—S bond and the S/C1/C4 plane of the THT ligand is 104.7° for S1 and 107.5° for S2. This tilting of the THT ligands corresponds to a pure sp^3-hybridization of the ligating S atoms. Examples for other chloridosilver(I) complexes with sulfur ligands are [AgCl(detu)$_3$] [detu = N,N'-diethylthiourea; Ag—S = 2.554 (1)–2.593 (1) Å; Bowmaker *et al.*, 2010] and [AgCl(9S3)] [9S3 = 1,4,7-trithiacyclononane; Ag—S = 2.598 (1)–2.618 (1) Å; Blower *et al.*, 1989], where similar Ag—S distances were observed.

In the title compound, the closest intermolecular contact is Cl···C4($-x, 1 - y, -z$) at 3.627 (9) Å, but the CH$_2$ group is not in a proper orientation for a potential C—H···Cl bonding interaction (C4—H4A···Cl = 114°, C4—H4B···Cl = 81°).

Synthesis and crystallization

A suspension of 0.72 g (5 mmol) of powdered silver(I) chloride in 5 ml of THT was refluxed for three h and then filtered. The resulting clear solution was layered with 10 ml of *n*-hexane at r.t. and then stored at −18°C. Colorless needle-like crystals were formed within a few days. When isolated
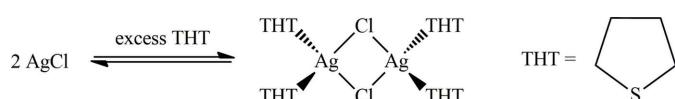
Figure 2
Reaction scheme.

Table 1
Experimental details.

Crystal data	
Chemical formula	[Ag$_2$Cl$_2$(C$_4$H$_8$S$_2$)$_4$]
M_r	639.29
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	200
a, b, c (Å)	6.1921 (8), 9.9443 (13), 10.3761 (12)
α, β, γ (°)	114.710 (9), 102.121 (10), 92.239 (11)
V (Å^3)	561.66 (13)
Z	1
Radiation type	Mo $K\alpha$
μ (mm^{-1})	2.35
Crystal size (mm)	0.50 × 0.05 × 0.05
Data collection	
Diffractometer	Stoe IPDS 2T
Absorption correction	Numerical (*X-AREA* and *X-RED*; Stoe & Cie, 2002)
T_{min}, T_{max}	0.398, 0.910
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3765, 1954, 1314
R_{int}	0.094
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.050, 0.125, 0.88
No. of reflections	1954
No. of parameters	109
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	1.39, −1.53

Computer programs: *X-AREA* and *X-RED* (Stoe & Cie, 2002), *SHELXL2014* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 1999) and *publCIF* (Westrip, 2010).

from the mother liquor, these slowly decompose under THT loss even at −70°C, and readily above 0°C or when treated with organic solvents. The reaction scheme is shown in Fig. 2.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

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full crystallographic data

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Crystal data
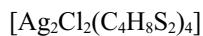
$[Ag_2Cl_2(C_4H_8S_2)_4]$	$Z = 1$
$M_r = 639.29$	$F(000) = 320$
Triclinic, $P\bar{1}$	$D_x = 1.890$ Mg m^{-3}
$a = 6.1921$ (8) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 9.9443$ (13) Å	Cell parameters from 5660 reflections
$c = 10.3761$ (12) Å	$\theta = 4.0$–29.2°
$\alpha = 114.710$ (9)°	$\mu = 2.35$ mm^{-1}
$\beta = 102.121$ (10)°	$T = 200$ K
$\gamma = 92.239$ (11)°	Needle, colorless
$V = 561.66$ (13) Å^3	$0.50 \times 0.05 \times 0.05$ mm

Data collection

Stoe IPDS 2T diffractometer	1954 independent reflections
Radiation source: fine-focus sealed tube	1314 reflections with $I > 2\sigma(I)$
area detector scans	$R_{int} = 0.094$
Absorption correction: numerical (X-AREA and X-RED; Stoe & Cie, 2002)	$\theta_{max} = 25.0°$, $\theta_{min} = 4.0°$
$T_{min} = 0.398$, $T_{max} = 0.910$	$h = -7 \rightarrow 7$
3765 measured reflections	$k = -11 \rightarrow 11$
	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.050$	H-atom parameters constrained
$wR(F^2) = 0.125$	$w = 1/[\sigma^2(F_o^2) + (0.0669P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.88$	
1954 reflections	$(\Delta/\sigma)_{max} < 0.001$
109 parameters	$\Delta\rho_{max} = 1.39$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -1.53$ e Å^{-3}
Primary atom site location: heavy-atom method	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. The H atoms of the THT ligands were fixed geometrically and refined using a riding model with U(H) = 1.20 U_{eq}(C). C—H distances were constrained to 0.99 Å.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.3137 (14)	0.1602 (9)	−0.3354 (9)	0.0357 (19)
H1B	0.4641	0.1706	−0.2730	0.043*
H1A	0.2860	0.0636	−0.4241	0.043*
C2	0.2946 (13)	0.2885 (10)	−0.3764 (10)	0.037 (2)
H2B	0.3729	0.2756	−0.4538	0.045*
H2A	0.3599	0.3845	−0.2902	0.045*
C3	0.0462 (15)	0.2851 (11)	−0.4317 (10)	0.045 (2)
H3B	−0.0119	0.1988	−0.5287	0.054*
H3A	0.0178	0.3779	−0.4419	0.054*
C4	−0.0682 (13)	0.2715 (10)	−0.3204 (9)	0.037 (2)
H4B	−0.2210	0.2162	−0.3695	0.045*
H4A	−0.0781	0.3719	−0.2455	0.045*
C5	0.1488 (14)	0.1726 (10)	0.1715 (10)	0.039 (2)
H5B	0.0765	0.1561	0.2412	0.047*
H5A	0.0342	0.1489	0.0798	0.047*
C6	0.3284 (17)	0.0802 (12)	0.1422 (17)	0.077 (4)
H6B	0.2843	−0.0172	0.1408	0.093*
H6A	0.3501	0.0608	0.0444	0.093*
C7	0.5338 (16)	0.1515 (11)	0.2503 (13)	0.057 (3)
H7B	0.6596	0.1120	0.2077	0.069*
H7A	0.5380	0.1268	0.3338	0.069*
C8	0.5628 (12)	0.3170 (9)	0.3049 (8)	0.0320 (18)
H8B	0.6702	0.3488	0.2610	0.038*
H8A	0.6197	0.3668	0.4128	0.038*
S1	0.1020 (3)	0.1702 (2)	−0.2355 (2)	0.0345 (5)
S2	0.2882 (3)	0.3662 (2)	0.2509 (2)	0.0306 (5)
Cl	0.2644 (3)	0.6363 (2)	−0.0082 (2)	0.0339 (5)
Ag	0.29919 (12)	0.39288 (8)	0.01788 (7)	0.0394 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.036 (4)	0.030 (5)	0.035 (4)	0.012 (4)	0.007 (4)	0.009 (4)
C2	0.032 (4)	0.050 (6)	0.039 (5)	0.005 (4)	0.014 (4)	0.026 (4)
C3	0.050 (5)	0.057 (6)	0.035 (5)	0.020 (5)	0.009 (4)	0.026 (5)
C4	0.027 (4)	0.047 (5)	0.034 (5)	0.013 (4)	0.002 (4)	0.016 (4)
C5	0.034 (4)	0.042 (5)	0.047 (5)	0.001 (4)	0.005 (4)	0.029 (4)
C6	0.051 (7)	0.032 (6)	0.122 (11)	0.009 (5)	0.007 (7)	0.014 (7)
C7	0.047 (6)	0.042 (6)	0.082 (8)	0.027 (5)	0.006 (5)	0.028 (6)
C8	0.028 (4)	0.038 (5)	0.027 (4)	0.002 (4)	−0.004 (3)	0.016 (4)
S1	0.0374 (11)	0.0337 (12)	0.0384 (12)	0.0066 (9)	0.0128 (9)	0.0197 (10)
S2	0.0335 (11)	0.0329 (11)	0.0301 (10)	0.0121 (9)	0.0089 (8)	0.0170 (9)
Cl	0.0343 (10)	0.0353 (11)	0.0410 (11)	0.0134 (9)	0.0130 (9)	0.0227 (10)
Ag	0.0508 (4)	0.0415 (4)	0.0340 (4)	0.0131 (3)	0.0097 (3)	0.0240 (3)

Geometric parameters (Å, º)

C1—C2	1.506 (11)	C7—C8	1.489 (12)
C1—S1	1.816 (9)	C8—S2	1.827 (7)
C2—C3	1.518 (12)	S1—Ag	2.623 (2)
C3—C4	1.524 (12)	S2—Ag	2.5541 (19)
C4—S1	1.826 (7)	Cl—Ag	2.5581 (19)
C5—C6	1.470 (14)	Cl—Ag[i]	2.748 (2)
C5—S2	1.837 (9)	Ag—Cl[i]	2.748 (2)
C6—C7	1.430 (15)		
C2—C1—S1	105.2 (5)	C8—S2—C5	93.4 (4)
C1—C2—C3	105.4 (7)	C8—S2—Ag	103.5 (3)
C2—C3—C4	107.4 (6)	C5—S2—Ag	100.4 (3)
C3—C4—S1	106.6 (5)	Ag—Cl—Ag[i]	79.35 (5)
C6—C5—S2	104.7 (7)	S2—Ag—Cl	123.95 (7)
C7—C6—C5	111.7 (10)	S2—Ag—S1	118.30 (7)
C6—C7—C8	112.4 (7)	Cl—Ag—S1	107.93 (7)
C7—C8—S2	106.7 (6)	S2—Ag—Cl[i]	101.61 (6)
C1—S1—C4	93.7 (4)	Cl—Ag—Cl[i]	100.65 (5)
C1—S1—Ag	100.2 (3)	S1—Ag—Cl[i]	98.94 (7)
C4—S1—Ag	99.8 (3)		
S1—C1—C2—C3	−44.4 (8)	C2—C1—S1—Ag	−76.7 (6)
C1—C2—C3—C4	48.3 (9)	C3—C4—S1—C1	3.1 (7)
C2—C3—C4—S1	−29.5 (9)	C3—C4—S1—Ag	104.1 (6)
S2—C5—C6—C7	34.5 (12)	C7—C8—S2—C5	3.3 (7)
C5—C6—C7—C8	−34.4 (15)	C7—C8—S2—Ag	−98.2 (6)
C6—C7—C8—S2	16.3 (12)	C6—C5—S2—C8	−20.9 (8)
C2—C1—S1—C4	23.9 (6)	C6—C5—S2—Ag	83.5 (8)

Symmetry code: (i) $-x+1, -y+1, -z$.