The uncoordinated ring of the η^6-tetralin ligand is disordered over two envelope conformations, with C2—C3 and C2'—C3' defining the two possible twist conformations of the ring (refined to occupancies of 0.664 and 0.336, respectively). The bond lengths within the C1—C2—C3—C4 and C1—C2'—C3'—C4 chains were restrained during refinement, and atoms C2, C2', C3 and C3' were refined isotropically.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1994). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *PATTY* in *DIRDIF92* (Beurskens et al., 1992). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Tetraphenylphosphonium tetrakis(1-methyl-1,2,3,4-tetrazole-5-thiolato-S)-aurate(III) hemihydrate

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Abstract

The tetraphenylphosphonium salt of tetrakis(1-methyl-1,2,3,4-tetrazole-5-thiolato)aurate(III) crystallizes as an H_2O hemisolvate, $(C_{24}H_{20}P)[Au(C_2H_3N_4S)_4]\cdot0.5H_2O$, in the monoclinic $C2/c$ space group, with the Au atom situated on an inversion centre. The tetrazole rings are arranged almost orthogonally with respect to the square coordination sphere. Au—S—C angles of 106.2 (1) and 107.1 (1)° were found.

Comment

As part of our systematic work on gold compounds, we studied the reaction of tetrachloroaurate(III) with sodium 1-methyl-1,2,3,4-tetrazole-5-thiolate (NaSmetetraz). The gold(I) anion $[Au(Smetetraz)_2]^-$ is obtained when the reaction is performed in methanol. Considerable amounts of the $[Au^{III}(Smetetraz)_4]^-$ anion can be obtained when the reaction is carried out in water and a bulky cation is added immediately after mixing the reactants. The red precipitates obtained in this way contain impurities of the Au^I complex which can be removed by recrystallization from common organic solvents. Following this route, we have prepared the tetraphenylarsonium and tetraethylammonium salts of $[Au(Smetetraz)_4]^-$ (Abram et al., 1998). A pure sample of the title compound, (I), was obtained via a two-phase reaction, where solid NaSmetetraz·xH_2O was mixed with a solution of $(Ph_4P)[AuCl_4]$ in CH_2Cl_2. The insolubility of the sodium salt avoids an excess of the

(I)
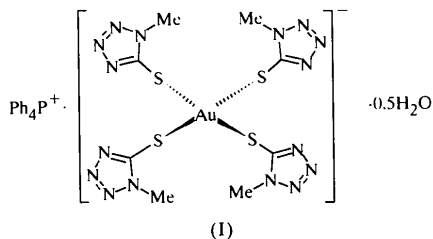
ligand in solution and gives (Ph$_4$P)[Au(Smetetraz)$_4$] in almost quantitative yield.

The Au atom has a square coordination sphere (Fig. 1), with Au—S distances of 2.352(1) and 2.356(1) Å. The ligands clearly have thiolate character, which is indicated by the S—C bond lengths of 1.735(3) and 1.736(3) Å, and the C—S—Au angles of 106.2(1) and 107.1(1)°. The heterocyclic rings are almost orthogonal to the coordination sphere of the metal, with interplanar angles of 83.0(1) and 88.2(1)°. However, an angle of 12.6(2)° was found between the Au/S1/C2 and Au/S11/C12 planes.

The Au atom in (Ph$_4$P)[Au(Smetetraz)$_4$], as in the isotypic tetraphenylarsonium salt of the same complex anion (Nöth *et al.*, 1998), occupies a centre of inversion. Consequently, two of the methyl groups of the ligands are arranged above and below the AuS$_4$ plane. This is in contrast to the situation in (Et$_4$N)[Au(Smetetraz)$_4$], which crystallizes in a tetragonal system and where the methyl substituents are all situated on the same side of the coordination plane (Abram *et al.*, 1998).

A disordered water molecule with a site occupancy of 0.5 is located at 0,0,0. The distances between the O atom and symmetry-related positions of N14, S1 and N15 lying in the range 2.6–2.8 Å suggest hydrogen bonds; this has been confirmed by calculations with the program *HYDROGEN* (Nardelli, 1999) by one of the referees of this paper, deriving water H-atom coordinates of −0.0462, −0.0272, −0.0048 and 0.0091, 0.0449, −0.0227.
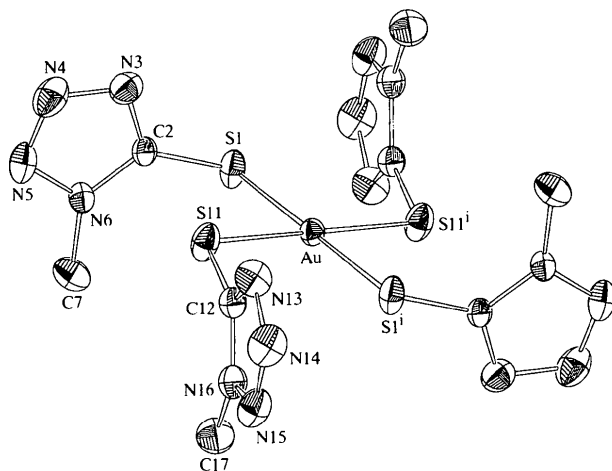

Fig. 1. *ZORTEP* diagram (Zsolnai, 1997) of the [Au(Smetetraz)$_4$]$^-$ anion, showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity. [Symmetry code: (i) $\frac{1}{2} - x$, $\frac{1}{2} - y$, $-z$.]

Experimental

(Ph$_4$P)[AuCl$_4$] (68 mg, 0.1 mmol) was dissolved in about 10 ml of CH$_2$Cl$_2$ and mixed with an approximate tenfold excess of solid NaSmetetraz·*x*H$_2$O. The mixture was stirred

for 10 h and the red solution was separated from the insoluble solid. Methanol (10 ml) was added and red needles of the title compound precipitated upon slow evaporation of the solvent; the yield was almost quantitative. Elemental analysis: C 38.92, H 3.85, N 22.14%; C$_{32}$H$_{33}$AuN$_{16}$O$_{0.5}$PS$_4$ requires: C 38.21, H 3.82, N 22.29%. FAB$^-$ MS: *m/z* 658 (100%, *M$^-$*).

Crystal data

(C$_{24}$H$_{20}$P)[Au(C$_2$H$_3$N$_4$S)$_4$]· 0.5H$_2$O	Mo $K\alpha$ radiation λ = 0.71073 Å
M_r = 1005.91	Cell parameters from 25
Monoclinic	reflections
C2/c	θ = 9.45–13.34°
a = 18.460(4) Å	μ = 4.145 mm^{-1}
b = 6.5520(5) Å	T = 208(2) K
c = 32.603(7) Å	Needle
β = 103.34(1)°	0.40 × 0.15 × 0.10 mm
V = 3836(1) Å^3	Red
Z = 4	
D_x = 1.740 Mg m^{-3}	
D_m not measured	

Data collection

Enraf–Nonius CAD-4 diffractometer	R_{int} = 0.023 θ_{max} = 26.97°
ω scans	$h = -23 \rightarrow 22$
Absorption correction:	$k = -1 \rightarrow 8$
ψ scan (*PLATON*; Spek, 1998)	$l = -1 \rightarrow 41$ 3 standard reflections
T_{min} = 0.425, T_{max} = 0.661	every 300 reflections
5168 measured reflections	frequency: 60 min
4177 independent reflections	intensity decay: 10%
3214 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max}$ = 0.001
$R[F^2 > 2\sigma(F^2)]$ = 0.024	$\Delta\rho_{max}$ = 0.565 e Å^{-3}
$wR(F^2)$ = 0.060	$\Delta\rho_{min}$ = −0.649 e Å^{-3}
S = 1.056	Extinction correction: none
4177 reflections	Scattering factors from
316 parameters	*International Tables for*
All H atoms refined	*Crystallography* (Vol. C)
$w = 1/[\sigma^2(F_o^2) + (0.0281P)^2$ $+ 6.6510P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. *Selected geometric parameters (Å, °)*

Au—S11	2.352(1)	C2—N6	1.342(4)
Au—S1	2.356(1)	S11—C12	1.735(3)
S1—C2	1.736(3)	C12—N13	1.324(5)
C2—N3	1.315(5)	C12—N16	1.336(5)
S11—Au—S1	89.50(3)	C12—S11—Au	107.1(1)
C2—S1—Au	106.2(1)	N13—C12—S11	125.3(3)
N3—C2—S1	126.9(3)	N16—C12—S11	125.6(3)
N6—C2—S1	124.4(3)		

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *SET4* in *CAD-4 Software*. Data reduction: *HEL-ENA* (Spek, 1998). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*b*). Molecular graphics:

ZORTEP (Zsolnai, 1997). Software used to prepare material for publication: SHELXL97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1415). Services for accessing these data are described at the back of the journal.

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A trimeric aluminium alkoxide: methoxy-aluminium dichloride

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Abstract

The title compound, *cyclo*-tri-μ-methoxo-tris(dichloro-aluminium), $C_3H_9Al_3Cl_6O_3$ or $[Al_3Cl_6(CH_3O)_3]$, has been characterized. Based on a six-membered $[AlO]_3$ ring, the molecular structure is trimeric. The Al—O distances are significantly shorter than those found in structurally related organoaluminium Lewis base–acid

complexes. This is a result of inductive effects due to the electronegative chlorine substituents bonded to the Al atoms.

Comment

Aluminium alkoxides, $[R_2Al(\mu\text{-}OR')]_n$, are of interest as potential catalysts, especially for the ring-opening polymerization of lactone rings (Inoue & Aida, 1993). They may form dimeric or trimeric species (Ouzounis *et al.*, 1983). Furthermore, complexes of the formula $[Me_2Al(\mu\text{-}OR')]_n$ have been found as equilibrium mixtures of trimers and dimers (Rogers *et al.*, 1992). We report here the synthesis and crystal structure of the related aluminium chloride $[Cl_2Al(\mu\text{-}OMe)]_3$, (I).

(I)
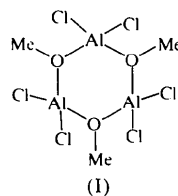
Compound (I) contains a six-membered skeleton composed of three Al and three methoxy O atoms. The average O—Al—O and Cl—Al—Cl angles of 98.5 and 114.9°, respectively, show the distortion of the tetrahedron around the Al atoms. The O atoms are surrounded in a nearly planar fashion. The average of the endocyclic Al—O—Al angle is 122.2°. The $[AlO]_3$ ring puckering analysis ($\varphi = 147.2°$ and $\theta = 90.2°$; Cremer & Pople, 1975) indicates a slightly distorted twisted-boat conformation. The puckering parameters θ and φ are 90° and $(k \times 60 + 30)°$, respectively, for the idealized geometry (Boeyens, 1978). In contrast, $[^tBu_2Al(\mu\text{-}OH)]_3$ has been found to adopt a planar conformation, with significantly larger intra-ring angles at the O atom (142°) and Al···Al distances of 3.49 Å. This observation was explained as intramolecular *tert*-butyl–*tert*-butyl repulsion (Mason *et al.*, 1993). However, the average Al···Al distance is 3.16 Å in (I) and the ring conformation is probably the
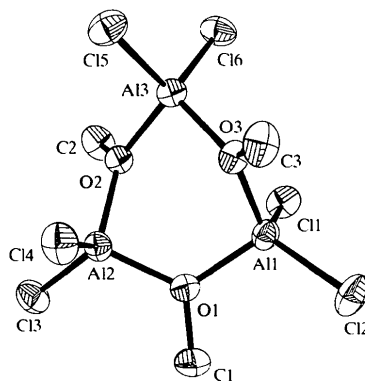

Fig. 1. The molecular structure of (I), with 50% probability displacement ellipsoids. H atoms have been omitted for clarity.