

Table 1. Selected geometric parameters (\AA , $^\circ$)

Cu1—O1'	1.9603 (19)	C4—C5	1.372 (3)
Cu1—N1'	1.9701 (18)	C5—C6	1.386 (3)
N1—N2	1.321 (2)	C7—O2	1.222 (3)
N1—C6	1.333 (3)	C7—O1	1.271 (3)
N2—C3	1.324 (3)	C7—C6	1.516 (3)
C3—C4	1.388 (3)	C8—O3	1.246 (3)
C3—C8	1.507 (3)	C8—O4	1.261 (3)

O1'—Cu1—N1' 82.26 (8)

Symmetry code: (i) $1-x, 1-y, 1-z$.Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
N2—H2...O1'	0.90	2.72	3.109 (3)	108
N2—H2...O3	0.90	2.36	2.688 (3)	102
O88—H88A...O1 ⁱⁱ	0.85	1.98	2.825 (3)	177
O88—H88B...O3 ⁱⁱⁱ	0.85	1.91	2.682 (3)	151
O99—H99A...O2 ^{iv}	0.85	1.97	2.804 (3)	168
O99—H99B...O4 ^v	0.85	1.97	2.694 (3)	143

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $1+x, y, z$; (iii) $2-x, 1-y, 1-z$; (iv) $1+x, y-1, z$; (v) $x-1, y, z$.

The crystal was lost before measurements for absorption corrections could be made. Other available crystals showed insignificant diffraction. The range of expected transmission factors is relatively small (0.76–0.87) due to the crystal size ($0.2 \times 0.1 \times 0.1$ mm) and the low value of μ (1.391 mm^{-1}). The H atoms of the aromatic ring were placed in calculated positions. The two H atoms associated with each of the water molecules and that on N2 were located from a difference Fourier synthesis and their positions improved with the HIMP facility of XP (Siemens, 1990).

Data collection: XSCANS (Siemens, 1991). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS97 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). Molecular graphics: XP.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1155). Services for accessing these data are described at the back of the journal.

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(1-Phenyl-1*H*-1,2,3,4-tetrazole-5-thiolato-*S*)-bis(triphenylphosphine)silver(I) methanol solvate

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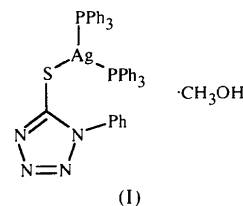
(Received 17 June 1998; accepted 6 January 1999)

Abstract

The title compound, $[\text{Ag}(\text{C}_7\text{H}_5\text{N}_4\text{S})(\text{C}_{18}\text{H}_{15}\text{P})_2] \cdot \text{CH}_3\text{OH}$, contains trigonal-planar silver coordinated to the thio-tetrazole ligand *via* sulfur. The presence of methanol, which hydrogen bonds to the tetrazole ring, weakens the donor capacity of the ring N atoms, preventing their interaction with silver.

Comment

The structure of $(\text{Ph}_3\text{P})_2\text{Ag}(\text{SCN}_4\text{Ph})$, solvated with a molecule of non-coordinating CH_2Cl_2 , has been reported recently (Noth *et al.*, 1998). We now report and compare the crystal structure of the same compound as its methanol solvate, which forms part of our general interest in the coordination chemistry of thiotetrazoles (Deeth *et al.*, 1992). The gross structure adopted by the title compound, (I), is essentially the same as that reported previously (Noth *et al.*, 1998); silver is coordinated in a trigonal-planar manner by two triphenylphosphine ligands and the thiotetrazole ligand is coordinated *via* its S atom. In the discussion below, the numbering scheme of Fig. 1 is applied to both determinations for clarity of comparison.



The key difference between the two determinations is the angle at sulfur and the role of the N4 atom. In the earlier work, the angle at sulfur is acute [$90.8(2)^\circ$], which allows close approach of N4 to silver (2.897 \AA) from above the P_2AgS plane (torsion angle N4—C37—S1—Ag1 117.5°). Although this does not perturb the planarity of the P_2SAg unit (sum of angles at Ag 359.9°), it was deemed responsible for the 4.8° (not 5.2° as cited) difference in the two P—Ag1—S1 angles.

In our work, in which the methanol O1 atom hydrogen bonds to the tetrazole N3 atom [O1—H1···N3 150 (4)°, H1···N3 2.14 (3) Å and N3···O1 2.899 (4) Å], the Ag—S—C angle opens to 99.1 (1)° and N4 moves away from the metal [3.216 (9) Å]. The tetrazole unit rotates to become almost coplanar with the P₂AgS plane [torsion angle N4—C37—S1—Ag1 -8.7 (3)°] on the side of P2, though remarkably this is the more acute side of the trigonal plane [P2—Ag1—S1 114.73 (3)°]. Thus, while the hydrogen bonding of methanol to the tetrazole ring appears to lower its basicity and cause a separation of the Ag1 and N4 atoms, it does not appear that a short Ag1···N4 interaction is responsible for the angular distortions about the metal.

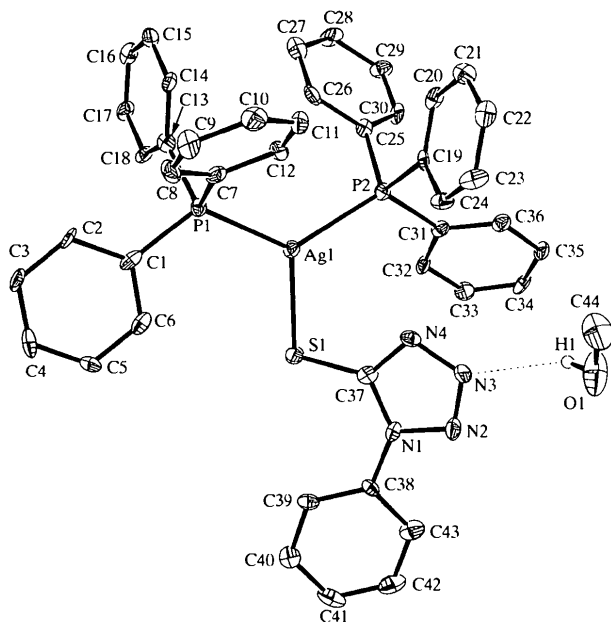


Fig. 1. ORTEX plot (McArdle, 1995) of the asymmetric unit of (I) showing the atom-labelling scheme. Ellipsoids are represented at the 30% probability level.

Experimental

The title compound was synthesized from tris(triphenylphosphine)silver chloride and ammonium 1-phenyl-1,2,3,4-tetrazole-5-thiolate in methanol. The product was separated from the ammonium chloride by-product by extraction into hot acetone. After removing the solvent *in vacuo*, the residue was recrystallized from methanol to yield the title compound (yield 53%).

Crystal data

[Ag(C₇H₅N₄S)(C₁₈H₁₅P)₂].CH₄O
M_r = 841.66
 Triclinic
 P1̄
 Mo *K*α radiation
 λ = 0.71069 Å
 Cell parameters from 25 reflections
 θ = 16.8–17.5°

a = 10.203 (2) Å
b = 13.047 (4) Å
c = 15.990 (5) Å
 α = 68.54 (3)°
 β = 85.85 (2)°
 γ = 76.48 (2)°
V = 1925.9 (9) Å³
Z = 2
D_x = 1.453 Mg m⁻³
D_m not measured

μ = 0.702 mm⁻¹
T = 170 (2) K
 Block
 0.2 × 0.2 × 0.2 mm
 Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
 θ/2θ scans
 Absorption correction: none
 7190 measured reflections
 6775 independent reflections
 5249 reflections with *I* > 2σ(*I*)
R_{int} = 0.017

θ_{max} = 25.01°
h = 0 → 12
k = -15 → 15
l = -18 → 19
 3 standard reflections every 80 reflections
 frequency: 150 min
 intensity decay: none

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.029
wR(*F*²) = 0.071
S = 1.015
 6772 reflections
 480 parameters
 H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.0378*P*)² + 0.7153*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.005
 Δρ_{max} = 0.76 e Å⁻³
 Δρ_{min} = -0.70 e Å⁻³
 Extinction correction: none
 Scattering factors from International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Ag1—P1	2.4503 (10)	N1—N2	1.365 (3)
Ag1—P2	2.4645 (10)	N1—C38	1.432 (4)
Ag1—S1	2.4909 (10)	N2—N3	1.279 (3)
S1—C37	1.716 (3)	N3—N4	1.359 (3)
N1—C37	1.363 (3)	N4—C37	1.335 (4)
P1—Ag1—P2	125.03 (3)	C37—N1—C38	133.1 (2)
P1—Ag1—S1	120.19 (3)	N2—N1—C38	118.4 (2)
P2—Ag1—S1	114.73 (3)	N3—N2—N1	106.1 (2)
C37—S1—Ag1	99.11 (10)	N2—N3—N4	112.2 (2)
C37—N1—N2	108.5 (2)	C37—N4—N3	106.1 (2)

H atoms were located from difference Fourier syntheses and were thereafter allowed to refine riding on their parent atoms, except for those of the methyl and hydroxyl groups, which were treated as rotating rigid groups.

Data collection: CAD-4-PC Software (Enraf–Nonius, 1992). Cell refinement: CELDIM in CAD-4-PC Software. Data reduction: XCAD (McArdle & Higgins, 1995). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEX (McArdle, 1995). Software used to prepare material for publication: SHELXL93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1275). Services for accessing these data are described at the back of the journal.

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[3,3'-Iminobis(*N,N*-dimethylpropylamine)](4'-methoxyflavonolato)zinc(II) perchlorate, [Zn(4'-MeOfla)(idpaH)]ClO₄†

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Abstract

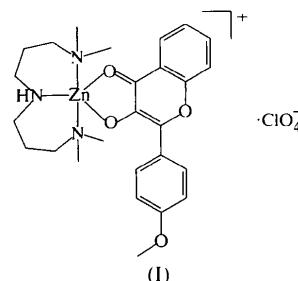
The title compound, [Zn(C₁₆H₁₁O₄)(C₁₀H₂₅N₃)]ClO₄, contains a cationic five-coordinate zinc(II) complex with distorted trigonal-bipyramidal geometry. Two N atoms of the tridentate 3,3'-iminobis(*N,N*-dimethylpropylamine) (idpaH) ligand and one O atom of the 4'-methoxyflavonolate (4'-MeOfla) ligand occupy basal positions, the other O atom of the flavonolate ligand and one N atom of the idpaH ligand being in apical positions.

Comment

Copper(I) and copper(II) complexes of flavonol, as structural and functional models of the Cu^{II}-containing dioxygenase quercetinase, have been reported (Speier *et al.*, 1990; Balogh-Hergovich *et al.*, 1991; Lippai *et al.*,

† Alternative name: [3,3'-iminobis(*N,N*-dimethylpropylamine-*N*)](2-(4-hydroxyphenyl)-4-oxo-4*H*-chromen-3-olato-*O*³,*O*⁴)zinc(II) perchlorate.

1997). Zinc and cadmium derivatives have also been prepared by electrochemical synthesis (Annan *et al.*, 1990). The flavonolate ligand (fla) coordinates metals through its 3-hydroxy and 4-carbonyl groups. We report here the preparation and crystal structure of a zinc(II) 4'-methoxyflavonolate, (I), with the nitrogen-containing ligand 3,3'-iminobis(*N,N*-dimethylpropylamine) in order to study model reactions of a non-redox metal system.



The geometry around the zinc(II) centre in compound (I) is approximately trigonal bipyramidal, with $\tau = 0.76$. For perfect square-pyramidal and trigonal-bipyramidal geometries, the values of τ are zero and unity, respectively, τ being an index of the degree of trigonality within the structural continuum between square-pyramidal and trigonal-bipyramidal geometries (Addison *et al.*, 1984). Two N atoms of the tridentate idpaH ligand, with Zn—N distances of 2.148 (4) and 2.115 (3) Å, and the O atom of the 3-hydroxy group of the 4'-methoxyflavonolate ligand occupy basal positions. The O atom of the 4-carbonyl group of the flavonolate and the N atom of the idpaH ligand, with a Zn—N distance of 2.151 (3) Å, are in apical positions.

The Zn—O bond distance of the 4-carbonyl O atom is shorter [Zn—O2 2.154 (3) Å] than that found in the only other known zinc(II) flavonolate complex, namely [Zn(flac)₂(tmeda)] [2.240 (1) Å; Annan *et al.*, 1990; tmeda is *N,N,N',N'*-tetramethylenediamine], and

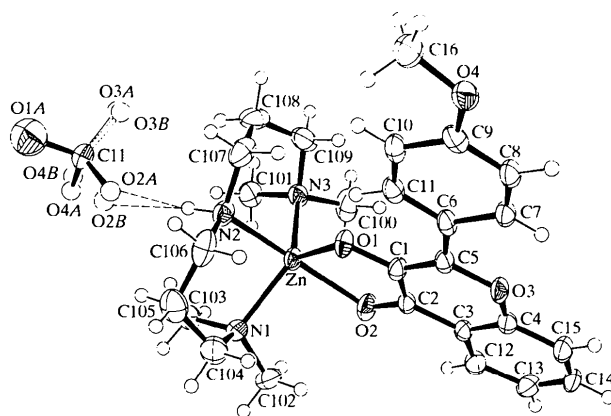


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids.