C24	0.8664 (5)	−0.0793 (7)	0.4081 (6)	0.088 (4)
C25	0.7752 (7)	−0.0533 (6)	0.3002 (6)	0.079 (3)
C26	0.6636 (6)	−0.0323 (5)	0.2509 (4)	0.058 (3)
C21	0.6433 (5)	−0.0373 (5)	0.3094 (5)	0.058 (3)
C22	0.7345 (6)	−0.0632 (5)	0.4172 (5)	0.059 (3)
C23	0.8461 (5)	−0.0842 (6)	0.4666 (4)	0.079 (3)
C27	0.5708 (12)	−0.0023 (10)	0.1329 (10)	0.080 (3)
Cl2	0.9670 (4)	−0.1252 (5)	0.5985 (4)	0.149 (2)
C1*A*	0.3271 (8)	0.1006 (9)	0.0501 (8)	0.057 (2)
C2*A*	0.2308 (7)	0.0955 (7)	−0.0655 (7)	0.097 (4)
F11	0.1268 (8)	0.1173 (15)	−0.1089 (9)	0.216 (7)
F12	0.2131 (11)	0.0046 (8)	−0.1131 (9)	0.158 (4)
F13	0.2306 (14)	0.1651 (10)	−0.1187 (10)	0.172 (5)
C1*B*	0.2963 (9)	0.0876 (10)	0.2075 (9)	0.065 (3)
C2*B*	0.1855 (9)	0.0841 (7)	0.1730 (8)	0.093 (4)
F21	0.0928 (7)	0.1099 (14)	0.0716 (9)	0.198 (6)
F22	0.1776 (9)	0.1544 (9)	0.2201 (10)	0.155 (5)
F23	0.1616 (10)	−0.0099 (7)	0.1870 (12)	0.181 (6)

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

Pd1—N11	1.938 (7)	Pd1···Pd2	2.8901 (13)
Pd1—C11	1.983 (5)	N11—O1	1.242 (9)
Pd1—O21	2.054 (7)	N11—N12	1.328 (11)
Pd1—O11	2.192 (8)	N12—C12	1.406 (9)
N11—Pd1—C11	80.8 (3)	O21—Pd1—O11	82.2 (3)
N11—Pd1—O21	176.4 (3)	C11—C16—C17	124.4 (7)
C11—Pd1—O21	101.9 (3)	C11—C12—N12	116.1 (6)
N11—Pd1—O11	94.9 (3)	C12—C13—Cl1	125.0 (5)
C11—Pd1—O11	174.4 (3)		

All H atoms were placed in calculated positions with fixed isotropic displacement parameters (U_{iso} = 0.080 Å^2). Some slightly disordered parts of the compound were refined with constraints or restraints. The C atoms in the phenyl rings were fitted to a regular hexagon with d = 1.39 Å. The C—F distance was restrained to 1.320 (1) Å. Some of the standard deviations are larger due to some libration of terminal groups, which is observed quite frequently with organometallic compounds.

Data collection: *EXPOSE* (Stoe & Cie, 1993). Cell refinement: *CELL* (Stoe & Cie, 1993). Data reduction: *CONVERT* (Stoe & Cie, 1993). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976; Larson *et al.*, 1986). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1060). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(1,3-Dimethyl-2,6-dioxo-2,3,6,7-tetrahydro-1*H*-purin-7-yl)(dimethylphenylphosphine)-gold(I)

AARNE PAJUNEN AND RAIKKO KIVEKÄS

Division of Inorganic Chemistry, University of Helsinki, PO Box 55, FIN-00014, Helsinki, Finland

ENRIQUE COLACIO AND RAFAEL CUESTA

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain

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Abstract

In [Au(PMe$_2$Ph)*T*], where *T* is the theophyllinate ligand, $C_7H_7N_4O_2^-$ (theophylline = 3,7-dihydro-1,3-dimethyl-1*H*-purine-2,6-dione), the Au atom is linearly coordinated by the P atom of the dimethylphenylphosphine ligand and the deprotonated N atom at position 7 of the theophyllinate ligand. Bond parameters involving Au are: Au—N 2.071 (9), Au—P 2.233 (3) Å and N—Au—P 177.5 (2)°.

Comment

Tertiary phosphines, P*R*$_3$, are the preferred ligands in the coordination chemistry of gold. In fact, much of the progress in gold chemistry in recent years has de-

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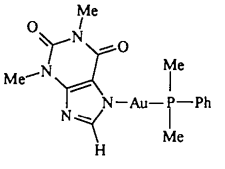
pended upon the use of phosphines as stabilizing auxiliary ligands. Gold(I) complexes with monodentate phosphines and oxopurines are of interest for the following reasons: (i) the gold(I) derivative auranofin [(2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranosato-*S*)triethylphosphinegold(I)], besides being a potent antiarthritic drug, has been proved to possess a significant *in vivo* antitumour activity in mice inoculated with lymphocytic leukemia P388 (Mirabelli *et al.*, 1985); (ii) phosphine–gold(I)–purine base derivatives might serve as model compounds for the interaction of gold(I) complexes with DNA in attempts to explain the mechanism of action of these complexes (Blank & Dabrowiak, 1984); (iii) a number of mononuclear (King, Khan, Staples & Fackler, 1992), binuclear (Jaw, Savas, Rogers & Mason, 1989) and polynuclear (Yan, Lai & Che, 1990) gold(I) compounds exhibit interesting photochemical and photophysical properties. As part of our effort to obtain structural information on gold(I) purine compounds, we undertook the X-ray crystal structure determination of the title compound, (I).



(I)

Reaction of theophylline (*T*) with $AuBr(PMe_2Ph)$ in a basic medium yields the 1:1 neutral complex $[Au(PMe_2Ph)T]$, in which the acidic imidazolic proton has been replaced. Thus, the IR spectrum of the complex shows no ν(N—H) bands at about 3000 cm^{-1} and the low-field signal for the proton is absent from the ^1H NMR spectrum. Furthermore, the H8 resonance is shifted upfield by 0.4 p.p.m. relative to that of H8 in theophylline, an observation that is consistent with the $AuPMe_2Ph$ group being bound to a deprotonated N-atom site in the imidazolic ring (Colacio *et al.*, 1989). Accordingly, the bands attributable to C=O, as well as the C=C and C=N stretching vibrations in the 1500–1700 cm^{-1} region, are lowered, since they are affected by the loss of the imidazolic proton. As expected, the ^{31}P NMR spectrum shows only one signal, at 7.14 p.p.m. In a basic medium theophylline and related oxopurine bases offer two N atoms, N7 and N9, for metal coordination, but in the solid state N7 is preferred over N9 (Cozak, Mardhy, Olivier & Beauchamp, 1986). The steric hindrance from the N3—CH_3 group may explain why N7 is favoured over N9. Where ligands lack the N3—CH_3 group, Au also coordinates to N9 as in, for example, adeninato(triphenylphosphine)gold(I) (Rosopulos, Nagel & Beck, 1985). In view of this, the coordination in the present complex would be expected to take place through N7. The results of our crystal structure determination confirm that this is so.

The title compound, (I), consists of discrete molecules. The Au atom exists with the expected linear coordination geometry, defined by the P atom of the dimethylphenylphosphine ligand and the deprotonated N7 atom of the theophyllinate ligand. The Au—P and Au—N7 distances in (I) and in the closely related $Au^I T$ complex of triphenylphosphine, (II) (Colacio *et al.*, 1989), are similar, but the P—Au—N7 angles are slightly different [177.5 (2) in (I) and 176.1 (2)° in (II)]. These values can be considered normal for bicoordinate Au^I.

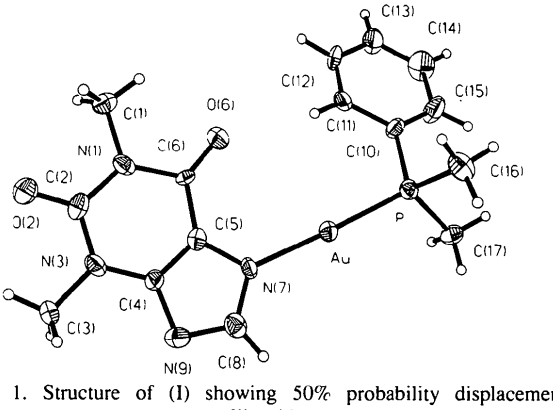


Fig. 1. Structure of (I) showing 50% probability displacement ellipsoids.

As expected, the nine atoms of the purine skeleton in (I) are coplanar, the greatest deviations from the mean-squares plane through the heterocyclic purine system being 0.030 (9) Å for N9. The exocyclic atoms O2, O6, C1 and C3 deviate from this plane by less than 0.05 Å. Similar planarity of the purine system and similar deviations of the exocyclic atoms have been reported for (II). The bond parameters of the theophyllinate ligand are as expected, and the values agree very well with those observed for the ligand in (II).

Coordination of Au to N7 results in an intramolecular Au···O6 contact of 3.333 (8) Å, which is similar to the value observed for (II) [3.317 (6) Å]. As reported earlier, significant *M*—O6 interaction should close the C5—N7—*M* angle and expand the C8—N7—Au angle (Cozak, Mardhy, Olivier & Beauchamp, 1986; Szalda, Kistenmacher & Marzilli, 1976). The angles at N7 in (I) show a similar trend to those in (II), where the angle C8—N7—Au [129.4 (4)°] is slightly greater than C5—N7—Au [125.9 (4)°]. On the other hand, the exocyclic bond angles at C6 in (I) indicate that O6 has moved away from Au so that the C5—C6—O6 angle is *ca* 10° greater than N1—C6—O6. These values, as well as the Au···O6 distance, which is 0.13 Å greater than the sum of the corresponding van der Waals radii (Bondi, 1964), show that the interaction between Au and O6 is very weak. The shortest intermolecular distance of 3.148 (10) Å to N9 at $2-x, -y, z+1/2$ is only *ca* 0.10 Å

shorter than the sum of the corresponding van der Waals radii (Bondi, 1964), which indicates that there is no significant interaction between the atoms.

The P—C bond lengths and Au—P—C and C—P—C angles in (I) are similar to those usually reported for phosphines (Clegg, 1978; Cookson & Tiekink, 1993) and do not require further discussion. Thus, changing the PPh_3 ligand of (II) to PMe_2Ph to obtain (I) has only a slight influence on the bond parameters of the P atom and does not appreciably modify the (theophyllinato)AuP moiety. The most interesting difference between (I) and (II) is in the packing. As expected, the larger size of the PPh_3 group in (II), compared with the PMe_2Ph group in (I), prevents short intermolecular contacts to Au in (II). In good accord with this, the shortest intermolecular contact to Au in (II) [3.300 (5) Å] is significantly greater than that in (I).

Experimental

The ligands theophylline and dimethylphenylphosphine were obtained from Aldrich and used without further purification. All manipulations were performed under nitrogen employing standard Schlenk techniques. The starting complex, [Au(PMe_2Ph)Br], was prepared by following a procedure similar to that reported by Colacio *et al.* (1989). To a stirred solution of [Au(PMe_2Ph)Br] (0.42 g, 1 mmol) in acetone (20 cm^3) was added a solution of theophylline (0.18 g, 1 mmol) in water (5 cm^3) containing 1 mol equivalent of KOH. The resulting solution was refluxed for 30 min in an N_2 atmosphere and then allowed to stand at room temperature for several hours, during which the white complex precipitated. The complex was filtered off, washed with water, acetone and diethyl ether, and dried *in vacuo* (yield 82%). Colourless crystals, stable in air, were obtained by slow evaporation of a solution of the complex in ethanol/water (10:1). [Au(PMe_2Ph)*T*]. Analysis: calculated for $C_{15}H_{18}N_4O_2PAu$ C 35.03, H 3.53, N 10.89, Au 38.30%; found C 35.30, H 3.64, Au 39.23%.

Microanalyses were performed with a Perkin–Elmer 240C analyser. Gold was determined thermogravimetrically with a Mettler TG-50 thermobalance in air, by using a heating rate of 5 K min^{-1}. Samples varied in weight from 9 to 10 mg. At 1023 K, the weight of the residue (metallic gold) became stable. IR spectra were recorded in the 4000–200 cm^{-1} range on a Perkin–Elmer 983G spectrophotometer, with samples embedded in KBr and polyethylene pellets. ^1H and ^{31}P NMR spectra of the complex dissolved in $(CD_3)_2SO$ were recorded on a Bruker AM300 spectrometer. ^1H NMR spectra were referenced internally to $SiMe_4$, and ^{31}P NMR spectra externally to H_3PO_4/D_2O (85:15 *v/v*).

Crystal data

[Au($C_7H_7N_4O_2$)($C_8H_{11}P$)]
M_r = 514.27
Orthorhombic
$Pna2_1$
a = 15.401 (7) Å
b = 18.228 (11) Å
c = 5.857 (3) Å
V = 1644.2 (15) $Å^3$
Z = 4
D_x = 2.077 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 20–25°
μ = 9.059 mm^{-1}
T = 193 (2) K
Prism
0.30 × 0.25 × 0.15 mm
Colourless

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction:
ψ scans (North, Phillips & Mathews, 1968)
T_{min} = 0.425, T_{max} = 1.000
1823 measured reflections
1823 independent reflections
1732 observed reflections [$I > 2\sigma(I)$]
θ_{max} = 26.48°
$h = 0 \rightarrow 19$
$k = 0 \rightarrow 22$
$l = 0 \rightarrow 7$
3 standard reflections monitored every 200 reflections
intensity decay: 0.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0351
$wR(F^2)$ = 0.0849
S = 1.120
1823 reflections
209 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0416P)^2 + 4.1271P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.020
$\Delta\rho_{max}$ = 1.54 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.98 e $Å^{-3}$
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0013 (3)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983) parameter = 0.02 (2)

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

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Au	0.83139 (2)	−0.05414 (2)	0.4995 (2)	0.0227 (2)
P	0.7592 (2)	−0.1422 (2)	0.6842 (6)	0.0222 (6)
O2	0.8321 (5)	0.1929 (5)	−0.4154 (17)	0.035 (2)
O6	0.7224 (5)	0.0164 (4)	0.0596 (15)	0.031 (2)
N1	0.7800 (5)	0.1036 (5)	−0.1797 (20)	0.025 (2)
N3	0.9172 (5)	0.1572 (5)	−0.1229 (19)	0.026 (2)
N7	0.8932 (5)	0.0299 (5)	0.3257 (19)	0.023 (2)
N9	0.9949 (6)	0.1128 (5)	0.2160 (19)	0.030 (2)
C1	0.7019 (7)	0.1008 (6)	−0.321 (3)	0.029 (3)
C2	0.8424 (7)	0.1543 (7)	−0.248 (2)	0.027 (3)
C3	0.9841 (7)	0.2100 (7)	−0.182 (3)	0.038 (3)
C4	0.9258 (7)	0.1141 (6)	0.067 (2)	0.023 (3)
C5	0.8645 (8)	0.0648 (6)	0.132 (2)	0.025 (3)
C6	0.7833 (5)	0.0566 (5)	0.016 (5)	0.019 (2)
C8	0.9713 (8)	0.0597 (6)	0.364 (3)	0.029 (3)
C10	0.6418 (7)	−0.1289 (6)	0.677 (2)	0.026 (2)
C11	0.6061 (6)	−0.0834 (5)	0.503 (4)	0.028 (2)
C12	0.5185 (8)	−0.0737 (6)	0.495 (5)	0.040 (3)
C13	0.4625 (7)	−0.1048 (7)	0.656 (3)	0.038 (3)
C14	0.4987 (8)	−0.1517 (8)	0.818 (3)	0.051 (4)
C15	0.5895 (8)	−0.1634 (8)	0.831 (3)	0.047 (4)
C16	0.7765 (8)	−0.2356 (6)	0.581 (2)	0.035 (3)
C17	0.7889 (7)	−0.1499 (7)	0.984 (3)	0.033 (3)

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

Au—N7	2.071 (9)	N3—C2	1.368 (15)
Au—P	2.233 (3)	N3—C4	1.367 (14)
P—C10	1.824 (11)	N3—C3	1.452 (13)
P—C16	1.827 (11)	N7—C8	1.338 (14)
P—C17	1.82 (2)	N7—C5	1.38 (2)
O2—C2	1.215 (15)	N9—C8	1.35 (2)
O6—C6	1.218 (12)	N9—C4	1.378 (14)

N1—C2	1.392 (14)	C4—C5	1.357 (15)
N1—C6	1.43 (2)	C5—C6	1.43 (2)
N1—C1	1.462 (14)		
N7—Au—P	177.5 (2)	C5—N7—Au	126.9 (7)
C10—P—C16	105.1 (5)	C8—N9—C4	102.2 (9)
C10—P—C17	106.3 (6)	O2—C2—N3	121.3 (11)
C16—P—C17	102.2 (6)	O2—C2—N1	121.8 (11)
C10—P—Au	112.8 (4)	N3—C2—N1	116.8 (10)
C16—P—Au	115.9 (4)	C5—C4—N3	122.7 (10)
C17—P—Au	113.4 (4)	C5—C4—N9	110.4 (10)
C2—N1—C6	127.1 (9)	N3—C4—N9	126.9 (10)
C2—N1—C1	115.2 (10)	C4—C5—N7	108.3 (10)
C6—N1—C1	117.6 (9)	C4—C5—C6	123.1 (13)
C2—N3—C4	119.7 (9)	N7—C5—C6	128.6 (12)
C2—N3—C3	119.7 (10)	O6—C6—C5	129.7 (19)
C4—N3—C3	120.4 (10)	O6—C6—N1	119.9 (14)
C8—N7—C5	103.9 (10)	C5—C6—N1	110.3 (10)
C8—N7—Au	129.1 (8)	N7—C8—N9	115.2 (11)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1993*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1194). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3,5-Dimethoxycarbonyl-2,6-dimethyl-4-(2-nitrosophenyl)pyridine and Dichlorobis[3,5-dimethoxycarbonyl-2,6-dimethyl-4-(2-nitrophenyl)pyridine]copper(II)

KRISTIN R. ROWAN AND ELIZABETH M. HOLT

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078, USA

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Abstract

Two decomposition products of the calcium channel blocker nifedipine {the title compounds dimethyl 2,6-dimethyl-4-(2-nitrosophenyl)pyridine-3,5-dicarboxylate, $C_{17}H_{16}N_2O_5$, and dichlorobis[dimethyl 2,6-dimethyl-4-(2-nitrophenyl)pyridine-3,5-dicarboxylate-*N*]copper(II), $[CuCl_2(C_{17}H_{16}N_2O_6)_2]$}, have been found to exist in the solid state, with approximately perpendicular orientations of the pyridine and phenyl rings. Unlike in the parent compound, the ester groups are not coplanar with their pyridine ring, but the nitro and nitroso substituents are coplanar with their respective phenyl rings.

Comment

Nifedipine [3,5-dimethoxycarbonyl-2,6-dimethyl-4-(2-nitrophenyl)-1,4-dihydropyridine], (I), is an important calcium-channel antagonist of the dihydropyridine type, known to interact with the α_1 moiety of L-type calcium channels, regulating excitation–contraction coupling of cardiovascular tissues, *i.e.* the smooth muscle of the veins and arteries. Compounds of this class are currently being used in the treatment of a variety of cardiovascular disorders such as angina and hypertension (Triggle, Langs & Janis, 1989; Hurwitz, Partridge & Leach, 1991).

Nifedipine, like most derivatives of the 1,4-dihydropyridine class, undergoes photodecomposition processes. This reaction has been reported to be extremely wavelength sensitive and two decomposition products have been identified by spectroscopic methods. Exposure to UV radiation appears to cause aromatization of the dihydropyridine ring and reduction of the nitro group