Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1955 measured reflections
1955 independent reflections
1831 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 23.5°$
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 11$
$l = -11 \rightarrow 11$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0382$
$wR(F^2) = 0.1066$
$S = 1.046$
1951 reflections
256 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0921P)^2 + 0.1003P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.011$
$\Delta\rho_{\max} = 0.617$ e Å^{-3}
$\Delta\rho_{\min} = -1.162$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.019 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cu1—O1	1.885 (2)	O2—C13	1.271 (3)
Cu1—O2	1.932 (2)	O3—C11	1.192 (4)
Cu1—N1	1.962 (3)	O4—C13	1.223 (4)
Cu1—N2	1.995 (3)	C11—C12	1.506 (4)
Cu1—O5	2.523 (3)	C12—C13	1.481 (4)
O1—C11	1.286 (4)		
O1—Cu1—O2	92.13 (10)	C11—O1—Cu1	124.0 (2)
O1—Cu1—N1	169.00 (9)	C13—O2—Cu1	124.3 (2)
O2—Cu1—N1	95.78 (9)	O3—C11—O1	122.1 (3)
O1—Cu1—N2	91.51 (10)	O3—C11—C12	119.9 (3)
O2—Cu1—N2	172.70 (9)	O1—C11—C12	118.1 (3)
N1—Cu1—N2	79.81 (10)	C13—C12—C11	116.2 (2)
O1—Cu1—O5	100.46 (11)	O4—C13—O2	124.1 (3)
O2—Cu1—O5	95.12 (10)	O4—C13—C12	118.3 (3)
N1—Cu1—O5	86.45 (10)	O2—C13—C12	117.5 (3)
N2—Cu1—O5	90.44 (10)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H$\cdots A$	H$\cdots A$	$D\cdots A$	D—H$\cdots A$	H—$D\cdots A$
O6—H61$\cdots$O1$^{\rm i}$	2.13 (4)	2.850 (4)	173 (4)	5 (3)
O6—H62$\cdots$O3$^{\rm ii}$	2.10 (4)	2.737 (4)	169 (4)	8 (3)
O5—H52$\cdots$O4$^{\rm iii}$	2.12 (5)	2.743 (4)	154 (6)	19 (4)
O5—H51$\cdots$O6$^{\rm iv}$	2.08 (4)	2.811 (4)	170 (4)	7 (3)

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

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965).

The authors wish to dedicate this paper to the memory of the late Dr K. Venkatasubramanian, who pioneered the X-ray crystallographic work in this laboratory. We wish to acknowledge Professor P. Natarajan, Director of the Institute, for his encouragement.

Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry have been deposited with the IUCr (Reference: DE1039). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 195–197

Luminescent Tris(3-ethyl-1,5-diaza-3-azonia-7-phosphatricyclo[3.3.1.1^{3,7}]decane-*P*)gold(I) Tetraiodide Trihydrate, [(EtTPA)$_3$Au]I$_4$.3H$_2$O

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Abstract

The title complex, [Au(C$_8$H$_{17}$N$_3$P)$_3$]I$_4$.3H$_2$O, has the complex cation lying with its Au and associated I atom on a crystallographic threefold axis. The AuP$_3$ moiety has distorted trigonal-planar geometry [the Au atom is 0.336 (3) Å from the P$_3$ plane], with Au—P 2.334 (3), Au$\cdots$I 2.9129 (12) Å and P—Au—P 117.97 (3)°. The asymmetric unit also has one iodide ion and one water molecule in general positions, with O$\cdots$I distances [3.516 (2) and 3.576 (2) Å] consistent with O—H$\cdots$I hydrogen bonding.

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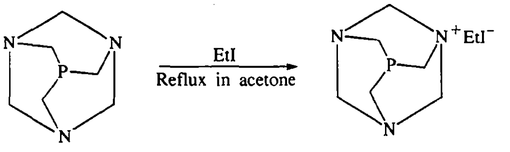
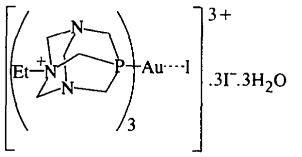
Comment

We have been studying the coordination of the 1,3,5-triaza-7-phosphaadamantane (TPA) ligand, to a gold(I) center to form the complexes Au*LX*, AuL_2X, AuL_3X and AuL_4X (where *L* = TPA; *X* = Cl, Br, I) (Assefa *et al.*, 1995). This ligand is of interest due to its small cone angle (102°; Darensburg & Daigle, 1975), which is similar to PMe_3, and its ability to form complexes that are both soluble and stable in aqueous solution. The three-coordinate complex, AuL_3X, is of special interest due to the observation that complexes containing gold(I) in a trigonal-planar arrangement can show luminescence both in the solid state and in solution (King, Khan, Staples & Fackler, 1992). The $[(TPA)_3Au]^+$ species has not been structurally characterized, but the title complex, $[(EtTPA)_3Au]I_4.3H_2O$, (3), containing the ethyl derivative of TPA as [EtTPA]I, (2), readily forms single crystals.



(1) (2)



(3)

The title structure consists of a gold(I) center coordinated to three EtTPA ligands in a distorted trigonal-planar arrangement (Fig. 1). The Au atom lies on the threefold axis. The Au—P bond length is 2.334 (3) Å, which is in the range found for complexes of this type (2.325–2.361 Å; Fackler, Staples & Assefa, 1994). The Au atom lies out of the P_3 plane by 0.336 (3) Å. One iodide ion is weakly coordinated to the gold(I) center on the threefold axis perpendicular to the P_3 plane at a distance of 2.9129 (12) Å. This distance is significantly longer than the 2.5–2.6 Å range usually observed for Au—I bond lengths (Bowmaker *et al.*, 1987). The structure is similar to that found for the methylated derivative $[(MeTPA)_3Au]I_4$ (Forward, Staples & Fackler, 1995).

The water molecule in the asymmetric unit is separated from the I2 ions by distances of 3.516 (2) and 3.576 (2) Å (to the I2 atom at equivalent position $\frac{2}{3}-x+y$, $\frac{1}{3}-y$, $\frac{1}{3}+z$). We were unable to locate the H atoms of the water molecule, but these separations are consistent with the presence of O—H···I hydrogen bonding. This type of hydrogen bonding has been observed previously in the literature and the O···I distance is similar to those found previously (3.2–3.8 Å; for example, see Fujiwara, Iwamoto & Yamamoto, 1984).

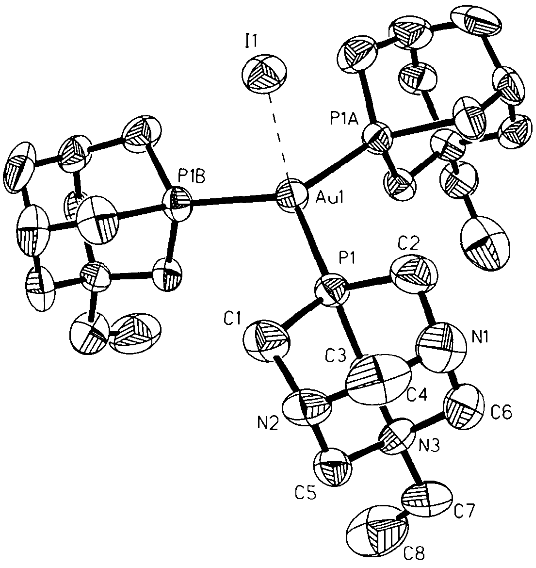


Fig. 1. A displacement ellipsoid plot (50% probability) of the $[(EtTPA)_3AuI]^{3+}$ moiety. The remaining iodide ions and water molecules are not shown for clarity.

Experimental

The [EtTPA]I ligand was synthesized in 92% yield according to an analogous procedure to that outlined for the synthesis of [MeTPA]I (Daigle & Pepperman, 1975). $[Au(Me_2S)Cl]$ (0.1 g, 3.40×10^{-4} mol) was stirred for 2 h with three equivalents of [EtTPA]I (0.319 g, 1.02×10^{-3} mol) in a CH_2Cl_2–H_2O solvent mixture (5 ml/5 ml). After the reaction was complete, the solvent was removed under reduced pressure and the white residue recrystallized from methanol. Single crystals were grown from a water solution of the product. The complex is luminescent in the solid state at 77 K. Excitation at 340 nm gives a yellow emission centered at 533 nm.

Crystal data

$[Au(C_8H_{17}N_3P)_3]I_4.3H_2O$
$M_r = 1313.23$
Trigonal
*R*3*c*
$a = 21.421$ (2) Å
$c = 15.063$ (2) Å
$V = 5985.5$ (9) Å^3
$Z = 6$
$D_x = 2.186$ Mg m^{-3}
D_m not measured

Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 20 reflections
$\theta = 6.5$–8.5°
$\mu = 6.940$ mm^{-1}
$T = 293$ (2) K
Plate
0.3 × 0.3 × 0.1 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.234$, $T_{max} = 0.500$
2116 measured reflections
1085 independent reflections

956 reflections with $I > 2\sigma(I)$
$R_{int} = 0.0508$
$\theta_{max} = 23.96°$
$h = -24 \rightarrow 0$
$k = 0 \rightarrow 24$
$l = 0 \rightarrow 17$
3 standard reflections every 120 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0245$
$wR(F^2) = 0.0565$
$S = 1.086$
1085 reflections
133 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0253P)^2 + 14.2616P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}} < 0.001$
$\Delta\rho_{\text{max}} = 1.006$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.511$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.016 (10)

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

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Au1	0	0	0.00000 (3)	0.0405 (2)
I1	0	0	0.19338 (7)	0.0546 (4)
I2	0.20575 (5)	−0.01867 (5)	0.29369 (8)	0.0644 (3)
P1	−0.00432 (15)	0.10561 (14)	−0.0223 (2)	0.0388 (6)
N1	−0.0748 (7)	0.1819 (7)	0.0010 (8)	0.070 (3)
N2	0.0562 (6)	0.2524 (5)	−0.0183 (7)	0.051 (2)
N3	−0.0221 (5)	0.1919 (5)	−0.1461 (6)	0.042 (2)
C1	0.0721 (8)	0.1955 (6)	0.0049 (8)	0.057 (3)
C2	−0.0757 (8)	0.1153 (8)	0.0286 (8)	0.063 (4)
C3	−0.0164 (6)	0.1244 (5)	−0.1376 (7)	0.043 (3)
C4	−0.0087 (11)	0.2445 (9)	0.0285 (10)	0.076 (4)
C5	0.0470 (7)	0.2573 (7)	−0.1116 (8)	0.050 (3)
C6	−0.0850 (7)	0.1848 (7)	−0.0909 (9)	0.058 (3)
C7	−0.0357 (8)	0.2038 (8)	−0.2389 (8)	0.064 (4)
C8	0.0159 (13)	0.2102 (11)	−0.3047 (12)	0.108 (7)
O1	0.2787 (8)	0.0154 (8)	0.5091 (10)	0.120 (5)

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

Au1—P1	2.334 (3)	N2—C5	1.43 (2)
Au1···I1	2.9129 (12)	N2—C1	1.46 (2)
P1—C2	1.813 (14)	N2—C4	1.49 (2)
P1—C3	1.831 (10)	N3—C7	1.477 (15)
P1—C1	1.845 (12)	N3—C3	1.514 (13)
N1—C6	1.41 (2)	N3—C6	1.525 (14)
N1—C4	1.44 (2)	N3—C5	1.53 (2)
N1—C2	1.48 (2)	C7—C8	1.44 (3)
P1^{i}—Au1—P1	117.97 (3)	C3—P1—C1	97.5 (5)
P1—Au1···I1	98.27 (7)	C2—P1—Au1	119.6 (4)
C2—P1—C3	99.0 (5)	C3—P1—Au1	115.4 (3)
C2—P1—C1	98.4 (6)	C1—P1—Au1	122.3 (5)

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

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL*/*PC* (Siemens, 1990). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1092). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 197–200

μ-Chloro-1:2κ^2*Cl*-trichloro-2κ^3*Cl*-(2,4-dimethyl-5,8-diazadec-4-ene-2,10-diamine-1κ^4*N*,*N*′,*N*″,*N*‴)copper(II)zinc(II)

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Abstract

The title compound, $[Cu(C_{10}H_{24}N_4)(\mu\text{-}Cl)ZnCl_3]$, is formed by the reaction of equimolar amounts of 3-azapentane-1,5-diamine, copper(II) chloride and zinc(II) chloride with excess 4-amino-4-methylpentan-2-one in methanol. The copper(II) ion is in a square-pyramidal coordination, with the tetradentate triamine mono-imine ligand in the basal plane (the mean Cu—N distance is 2.005 Å) and a Cl atom of a tetrachlorozincate ion axially coordinated, with a Cu—Cl distance of 2.6630 (7), a Cl—Zn distance of 2.3107 (7) Å and a Cu—Cl—Zn angle of 113.14 (2)°. The chloro-bridged