N22—C9	1.378 (5)	O1S—C1S	1.365 (6)
N22—C6	1.385 (5)	C11—O2	1.385 (7)
C1—C10^i	1.386 (5)	C11—O4	1.441 (8)
C1—C2	1.450 (5)	C11—O1^{ii}	1.478 (6)
C2—C3	1.370 (5)	C11—O3	1.513 (6)
C3—C4	1.444 (5)		
N21—Fe—N21^i	180.0	C2—C3—C4	107.2 (3)
N21—Fe—N22	89.36 (12)	N21—C4—C5	124.2 (3)
N21—Fe—O1A	90.77 (11)	N21—C4—C3	110.1 (3)
N22—Fe—O1A	91.33 (11)	C5—C4—C3	125.7 (3)
C1A—O1A—Fe	123.5 (2)	C6—C5—C4	126.6 (3)
C1—N21—C4	105.9 (3)	N22—C6—C5	124.5 (3)
C1—N21—Fe	126.1 (2)	N22—C6—C7	109.9 (3)
C4—N21—Fe	127.9 (2)	C5—C6—C7	125.6 (3)
C9—N22—C6	105.9 (3)	C8—C7—C6	107.1 (3)
C9—N22—Fe	126.7 (2)	C7—C8—C9	106.7 (3)
C6—N22—Fe	127.3 (2)	N22—C9—C10	124.3 (3)
N21—C1—C2	110.1 (3)	N22—C9—C8	110.4 (3)
C3—C2—C1	106.7 (3)	C10—C9—C8	125.3 (3)

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (ii) $-x, y, \frac{1}{2} - z$.

The perchlorate ion shows symmetry-imposed disorder and deviations from tetrahedral geometry, and could not be modelled satisfactorily. The anion was refined over four split positions with equal occupancies of 0.5. The hydroxy H atoms of both the methanol ligands and the methanol solvate molecules were not located.

Data collection: *P3 Diffractometer Program* (Siemens, 1989). Cell refinement: *P3 Diffractometer Program*. Data reduction: *XDISK* (Siemens, 1991). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL94* (Sheldrick, 1994). Molecular graphics: *XP* in *SHELXTL-Plus* (Siemens, 1994). Software used to prepare material for publication: *XCIF* in *SHELXTL-Plus*.

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Bis(1,3,5-triaza-7-phosphaadamantane-*P*)-gold(I) Chloride

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Abstract

The central Au atom in the title compound, $[Au(C_6H_{12}N_3P)_2]Cl$, lies on an inversion center and the twofold coordination is necessarily linear, with Au—P 2.261 (5) Å. The Cl$^-$ ion is in a general position with 0.5 occupancy; the shortest Au$\cdots$Cl distance is 3.224 (4) Å.
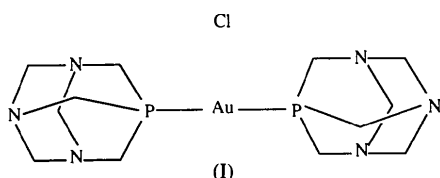
Comment

Linear two-coordinate cationic bisphosphine gold(I) complexes, (L_2Au^+), are thought to have little interaction between the counteranion and the Au atom. Recently, there has been an increase in the number of structures that show that three-coordinate gold(I) complexes do exist (see Table 3; for some examples see: Baenziger, Dittemore & Doyle, 1974; Muir, Muir & Arias 1982; Guggenberger, 1974). Gold(I) complexes with two weakly donating phosphines, such as PPh_3, appear to show this additional interaction more readily than those with the trialkylphosphines (Baenziger, Dittemore & Doyle, 1974; Muir, Muir & Arias 1982). For example, $(PPh_3)_2AuCl$ and $(PPh_3)_2AuSCN$ possess strong Au—Cl and Au—S interactions and a nearly planar geometry. No third ligand interaction is evident in the corresponding trialkylphosphine complexes. For the bisphosphine gold(I) xanthates reported recently (Assefa, Staples & Fackler, 1994), the P—Au—P angle is larger and the Au—S distance is smaller when the phosphine is PPh_3 than when it is the weakly more basic ligand CEP [CEP = tris(cyanoethyl)phosphine], even

though the cone angle of PPh_3 is larger than that of CEP (Khan, King, Fackler & Winpenny, 1993). Theoretical studies of the bisphosphine system suggest that electronic factors dictate the geometries observed in these systems and, therefore, the interaction of the Au atom with the anion.

Recently, we have been studying the effect that various phosphines have on the structural aspects of gold(I) complexes. 1,3,5-Triaza-7-phosphaadamantane (TPA) has been shown to be as strong a base as PMe_3 and to have a small cone angle of 102° (Darensbourg & Daigle 1975) which avoids any steric crowding which could prevent chloride coordination. Thus, electronic factors should control the coordination in $(TPA)_2AuX$ complexes.

Fig. 1 is a displacement ellipsoid drawing of the title molecule, (I), with our atom-labeling scheme. The

Cl

(I)

Au atom lies on an inversion center, which requires the Au coordination to be linear. There is no bonding between the Au atom and the disordered Cl^- ion; the shortest $Au\cdots Cl$ distance is 3.224(4) Å, which is substantially greater than the distances for the compounds listed in Table 3 where weak coordination is observed. The absence of $Au\cdots Cl$ interactions suggests that the TPA ligand is a stronger σ donor than the triphenylphosphine or CEP ligands. The Au—P distance of 2.261(5) Å is the shortest Au—P distance observed for the $[AuL_2]^+$ complexes listed in Table 3. This short distance also supports the idea that TPA is a strong σ-donor ligand.
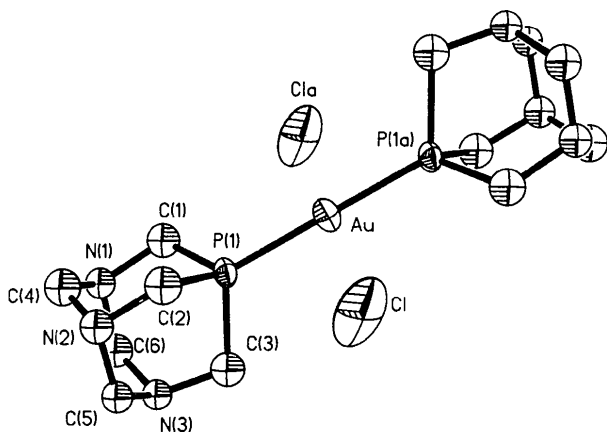

Fig. 1. Drawing of $(TPA)_2AuCl$ (50% probability ellipsoids) showing the labeling scheme and Cl atoms with an occupancy of 0.5 [the label a indicates the symmetry code (i) of Table 2].

Experimental

Crystals of the title compound, (I), were obtained from CH_3CN/acetone solution.

Crystal data

$[Au(C_6H_{12}N_3P)_2]Cl$	Mo $K\alpha$ radiation
$M_r = 546.7$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$P2_1/n$	reflections
$a = 5.992(1)$ Å	$\theta = 10-12.5°$
$b = 23.577(9)$ Å	$\mu = 8.505$ mm^{-1}
$c = 6.563(2)$ Å	$T = 293$ K
$\beta = 104.35(2)°$	Block
$V = 898.3(5)$ Å^3	$0.2 \times 0.1 \times 0.1$ mm
$Z = 2$	Colorless
$D_x = 2.02$ Mg m^{-3}	

Data collection

$R3m/E$ diffractometer	$R_{int} = 0.0241$
Wyckoff scans	$\theta_{max} = 22.5°$
Absorption correction:	$h = -6 \rightarrow 6$
ψ scans (Sheldrick, 1985)	$k = 0 \rightarrow 22$
$T_{min} = 0.558$, $T_{max} =$	$l = 0 \rightarrow 7$
0.980	3 standard reflections
1313 measured reflections	monitored every 97
1152 independent reflections	reflections
895 observed reflections	intensity decay: none
$[F_o^2 > 3\sigma(F_o^2)]$	

Refinement

Refinement on F	$w = 1/[\sigma^2(F_o) + 0.0046F_o^2]$
$R = 0.0585$	$(\Delta/\sigma)_{max} = 0.001$
$wR = 0.1103$	$\Delta\rho_{max} = 1.12$ e Å^{-3}
$S = 1.48$	$\Delta\rho_{min} = -2.38$ e Å^{-3}
895 reflections	Extinction correction: none
61 parameters	Atomic scattering factors
H atoms refined using a	from International Tables
riding model (C—H =	for X-ray Crystallography
0.96 Å)	(1974, Vol. IV)

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

U_{iso} for C and N; $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$ for Au, P and Cl.

	x	y	z	U_{iso}/U_{eq}
Au	0	1/2	1/2	0.043 (1)
Cl†	0.283 (4)	0.5245 (8)	0.978 (2)	0.109 (8)
P(1)	0.1902 (9)	0.4170 (2)	0.5063 (7)	0.030 (2)
N(1)	0.237 (3)	0.3076 (7)	0.357 (2)	0.038 (4)
N(2)	0.354 (3)	0.3208 (7)	0.749 (2)	0.040 (4)
N(3)	0.605 (3)	0.3590 (7)	0.523 (2)	0.035 (4)
C(1)	0.090 (4)	0.3607 (9)	0.311 (3)	0.045 (5)
C(2)	0.223 (4)	0.3733 (9)	0.746 (3)	0.048 (5)
C(3)	0.519 (3)	0.418 (1)	0.506 (3)	0.046 (5)
C(4)	0.240 (4)	0.2860 (9)	0.568 (3)	0.051 (5)
C(5)	0.585 (4)	0.3341 (8)	0.725 (3)	0.036 (4)
C(6)	0.473 (4)	0.320 (1)	0.359 (3)	0.045 (5)

† Occupancy = 0.5.

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

Au—P(1)	2.261 (5)	Au—P(1^i)	2.261 (5)
P(1)—Au—P(1^i)	180.0 (1)	P(1)—Au—Cl^i	89.8 (8)

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

Table 3. *Comparison of Au—P and Au—X distances in some bisphosphinegold(I) complexes*

Complex*	Au—P (Å)	Au—X (Å)	Reference
Au(PPh₃)₂Cl·½C₆H₆	2.334 (4), 2.323 (4)	2.500 (4)	Baenziger, Dittemore & Doyle (1974)
Au(PPh₃)₂Cl	2.336 (4), 2.317 (4)	2.533 (4)	Bowmaker, Dyason, Healy, Engelhardt, Pakawatchai & White (1987)
Au(PPh₃)₂SCN	2.349 (4), 2.346 (4)	2.468 (5)	Muir, Muir & Arias (1982)
Au(PPh₃)₂NO₃	2.314 (2), 2.309 (2)	–	Staples, King, Khan, Winpenny & Fackler (1993)
Au(PPh₃)₂PF₆	2.312 (4)	–	Staples, King, Khan, Winpenny & Fackler (1993)
Au(PCy₂Ph)₂Cl	2.324 (1), 2.300 (1)	2.744 (2)	Muir, Cuadrado, Muir & Barnes (1988)
Au(CEP)₂Cl	2.314 (2)	–	Khan, King, Fackler & Winpenny (1993)
Au(CEP)₂(S₂COEt)	2.306 (1), 2.310 (2)	2.745 (2) 2.934 (2)	Assefa, Staples & Fackler (1994)
Au(PPh₃)₂(S₂COEt)	2.349 (1), 2.315 (2)	2.530 (2) 3.112 (2)	Assefa, Staples & Fackler (1994)
Au(PBu₃)₂BPh₄	2.310 (3), 2.305 (4)	–	Staples, Fackler, Khan & Winpenny (1994)
Au(PCy₃)₂SCN	2.29 (1), 2.32 (1)	–	Muir, Muir & Lorca (1980)
[Au(PEt₃)₂][Au(MNT)₂]	2.315 (3), 2.311 (3)	–	Davila, Staples & Fackler (1994)
Au(PCy₃)₂Cl	2.321 (2)	–	Muir, Muir, Pulgar, Jones & Sheldrick (1985)
Au(PCy₃)₂PF₆	2.325 (6), 2.324 (6)	–	Cooper, Dennis, Henrick & McPartlin (1980)
Au(TPA)₂Cl	2.261 (5)	3.224 (4)	This work

*Cy = cyclohexyl; Ph = phenyl; Et = ethyl; Bu = n-butyl; CEP = cyanoethylphosphine; TPA = triazaphosphadamantane; MNT = maleonitriledithiolate [S(CN)C=C(CN)S]²⁻.

The crystal quality was below normal as seen from the profiles of several reflections. The data for some reflections were removed because of their asymmetric profiles. The poorer data set required that only the Au, P and Cl atoms could be successfully modelled anisotropically. The structure was solved by direct methods [*SHELXS*86 (Sheldrick, 1985); *SHELXTL-Plus* (Sheldrick, 1990)]. Full-matrix least-squares anisotropic refinement for Au, Cl and P, and isotropic refinement for all remaining non-H atoms was performed (*SHELXS*86 and *SHELXTL-Plus*). H atoms were placed in idealized positions with isotropic displacement parameters fixed at 0.08 Å².

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1043). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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cis-Dipyridine Complex of Bis(ω-nitroacetophenonato)manganese(II)

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Abstract

In the title compound, bis(ω-nitroacetophenonato-*O,O'*)-bis(pyridine)manganese(II), [Mn(C₈H₆NO₃)₂(C₅H₅N)₂], the ω-nitroacetophenonato (ω-nap) ligands chelate the manganese centre, forming a six-membered ring with a bite angle of 80.13 (11)°. The distance from the metal to the nitro O atom is longer than that from the