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Syntheses and Structural Characterization of Tetrahedral Four-Coordinate Gold(I) Complexes of 1,3,5-Triaza-7-phosphaadamantane. An Example of a Hydrogen-Bond-Directed Supramolecular Assembly

Jennifer M. Forward, Zerihun Assefa, Richard J. Staples, and John P. Fackler, Jr.*

Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University,
College Station, Texas 77843-3255

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The synthesis and structural characterization of water-soluble four-coordinate gold(I) complexes containing monodentate phosphine ligands are described. The ligands used are 1,3,5-triaza-7-phosphaadamantane (TPA) and its protonated and methylated derivatives, [HTPA]Cl and [MeTPA]I. Formation of the four-coordinate gold(I) species is favored by the small cone angle of the phosphine (102°) and its ability to form a hydrogen-bonded network between the nitrogen atoms of the ligand and solvent water molecules. The gold center in all four complexes has a nearly regular tetrahedral geometry with an average P−Au−P angle of 109.5°. $[(HTPA)_3(TPA)Au](PF_6)_4{\cdot}4H_2O{\cdot}CH_3CN$ **(1)** crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with cell constants $a = 20.719(3)$ Å, $b = 15.606(2)$ Å, $c = 17.854(2)$ Å, $\beta = 114.03(1)°$, and $Z = 4$. Refinement of 4977 reflections and 650 parameters yields $R = 0.0396$ and $R_w = 0.0500$. $[(TPA)_4Au]PF_6{\cdot}1.5HCl{\cdot}H_2O$ (**2**)**,** crystallizes in the monoclinic space group $C2/c$ (No. 15) with cell constants $a = 33.036(7)$ Å, $b = 11.212(2)$ Å, $c = 31.503(5)$ Å, $b = 137.58(1)°$, and $Z = 8$. Refinement of 3835 reflections and 470 parameters yields $R = 0.0351$ and $R_w = 0.0403$. $[(TPA)_4Au]Cl_4{\cdot}6H_2O$ (**3**) was characterized structurally in the cubic space group $Fd\bar{3}m$ (No. 227) with cell constants $a = b = c = 20.020(2)$ Å and $Z = 8$. Refinement of 290 reflections and 28 parameters yields $R = 0.0624$ and $R_w = 0.1291$. $[(MeTPA)_4Au](PF_6)_5{\cdot}2CH_3CN$ (**4**) crystallizes in the monoclinic space group $C2/c$ (No. 15) with cell constants $a = 23.337(3)$ Å, $b = 14.855(3)$ Å, $c = 35.317(5)$ Å, $b = 97.95(1)°$, and $Z = 8$. Refinement of 7840 reflections and 621 parameters yields $R = 0.0493$ and $R_w = 0.0698$.

Introduction

Although the preferred geometry of gold(I) complexes is linear, two-coordination at the gold center, examples of both trigonal planar and tetrahedral coordination have been reported.[1] Solution NMR studies have shown that addition of excess phosphine to $[AuL_2]^+$ (L = phosphine) can lead to the formation of the $[AuL_3]^+$ and $[AuL_4]^+$ species, but surprisingly few of these complexes have been structurally characterized.[2,3] In addition, the majority of the four-coordinate species that have been isolated contain either bidentate phosphines[4] or thiolate ligands.[5] Examples with monodentate phosphines are extremely rare, and a report in 1980 even suggested that tetrahedral $[AuL_4]^+$ complexes may not be attainable, at least at room temperature.[6] This proved not to be the case, however, when Elder[7] characterized the $[Au(PPh_2Me)_4](PF_6)$ complex in 1981 and showed it to have a nearly tetrahedral geometry at the gold center. As expected, the steric bulk of the phosphine plays a role as illustrated by the fact that, with a large cone angle phosphine such as PPh_3, the $[Au(PPh_3)_4](BPh_4)$ complex formed has a highly distorted structure containing an almost trigonal planar gold with the fourth phosphine weakly coordinated perpendicular to the P_3Au plane.[6]

We have been investigating the coordination of the 1,3,5-triaza-7-phosphaadamantane phosphine ligand (TPA) to a gold(I) center.[8,9] This ligand has a relatively small cone angle (102°), and by taking advantage of this reduced steric hindrance, we have been able to crystallize a series of stable four-coordinate gold(I) complexes that show a nearly regular tetrahedral geometry. This ligand is also of interest due to its solubility in aqueous solution and its ability to form hydrogen bonds with both counterions and water molecules. In addition, the TPA can be either protonated or methylated at one of the nitrogen sites to form [HTPA]Cl or [MeTPA]I, respectively (Scheme 1).

Experimental Section

All experiments were carried out under an atmosphere of dry nitrogen using standard Schlenk line techniques. The organic solvents were rigorously dried prior to use, and the water was deionized and doubly distilled. The TPA,[10] [HTPA]Cl,[10] and [MeTPA]I[11] ligands were prepared as reported in the literature, and the purity was checked by $^{31}P\{^1H\}$ NMR. The unprotonated TPA shows a singlet at −96.7 ppm, while [HTPA]Cl and [MeTPA]I give singlets at −89.5 and −86.93 ppm, respectively.

$^{31}P\{^1H\}$ NMR spectra were recorded using a Varian XL-400 spectrometer in D_2O/H_2O (1:10) at room temperature. Chemical shifts,

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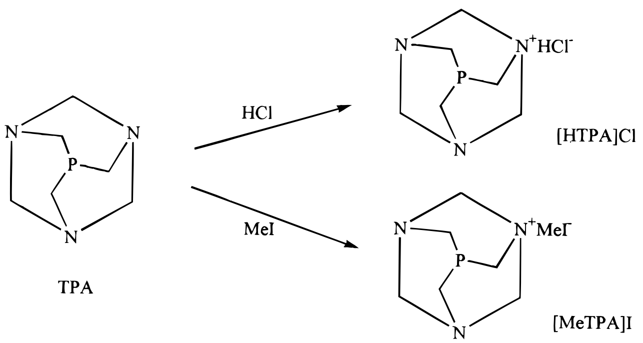
Table 1. Crystallographic Data

	$[(HTPA)_3(TPA)Au](PF_6)_4\cdot 4H_2O\cdot CH_3CN$ (**1**)	$[(TPA)_4Au]PF_6\cdot 1.5HCl\cdot 2H_2O$ (**2**)	$[(TPA)_4Au]Cl\cdot 6H_2O$ (**3**)	$[(MeTPA)_4Au](PF_6)_5\cdot 2CH_3CN$ (**4**)
chemical formula	$C_{26}H_{62}N_{13}O_4F_{24}P_8Au$	$C_{24}H_{54.5}H_{12}F_6P_5Cl_{1.5}AuO_2$	$C_{24}H_{60}AuClN_{12}O_6P_4$	$C_{32}H_{66}Au_{30}N_{14}P_9$
molecular weight	1521.11	1062.8	969.14	1692.68
crystal size, mm	0.6 × 0.3 × 0.2	0.2 × 0.1 × 0.1	0.3 × 0.2 × 0.2	0.3 × 0.2 × 0.2
crystal system	monoclinic	monoclinic	cubic	monoclinic
space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)	$Fd\bar{3}m$ (No. 227)[c]	$C2_1/c$ (No. 15)
a, Å	20.719(3)	33.036(7)	20.020(2)	23.337(3)
b, Å	15.606(2)	11.212(2)	20.020(2)	14.855(3)
c, Å	17.854(2)	31.503(5)	20.020(2)	35.317(5)
β, deg	114.03(1)	137.58(1)		97.95(1)
V, Å^3	5573(1)	7871.18(1)	8024(1)	12126(3)
Z	4	8	8	8
μ, mm·L	3.18	4.103	3.944	2.799
absorption correction	semiempirical	semiempirical	none	semiempirical
Dc, g cm^{-3}	1.813	1.794	1.604	1.854
temp, K	296	296	296	296
radiation (λ, Å)	graphite-monochromated Mo Kα (0.71073)			
R,[a] R_w[b]	0.0396, 0.0500	0.0351, 0.0403	0.0624, 0.1291	0.0493, 0.0698

[a] $R = ||F_o - |F_c||/\Sigma|F_o|$. [b] $R_w = \{[\ \Sigma w(|F_o - |F_c|)]/\Sigma w|F_o|\}^{1/2}$. [c] Space group not fully determined.

Scheme 1



in ppm, were referenced to an external standard of 85% H_3PO_4. ^1H NMR spectra in D_2O were recorded at ambient temperatures on a Varian XL-200 spectrometer.

X-ray structural analyses were performed on either a Nicolet R3m/E or CAD4 diffractometer employing Nicolet SHELXTL 5.1 and a Microvax II computer.

$[MeTPA]PF_6$. To 0.224g, 0.75 mmol of [MeTPA]I in 7mL of water, an equivalent of $NaPF_6$ (0.126g, 750 mmol) was added and a white precipitate formed almost immediately. The reaction was left to stir for thirty minutes and filtered and the precipitate was washed with cold water. Yield = 71%. $^{31}P\{^1H\}$ NMR = −84.2 ppm, 83.0 ppm (PF_6^-).

$[(HTPA)_3(TPA)Au](PF_6)_4\cdot 4H_2O\cdot CH_3CN$, 1. To a stirred suspension of (tht)AuCl (tht = tetrahydrothiophene) (0.10 g, 0.31 mmol) in 10 mL of CH_3CN/MeOH (1:2) was added 4 equiv of the protonated ligand [HTPA]Cl (0.241 g, 1.24 mmol) in one portion. A white precipitate was formed almost immediately. After stirring for 1 h, water was added dropwise until the precipitate completely disappeared (ca. 5 mL). The clear solution was then stirred for 30 min. Slow evaporation of the water at room temperature gave a white crystalline product that analyzed as $[(HTPA)_3(TPA)Au]Cl_4\cdot 4H_2O$ from a single crystal X-ray analysis. $^{31}P\{^1H\}$ NMR: −59.0 ppm (broad). This product was suspended in methanol, and $NaPF_6$ (0.634 g, 0.47 mmol) was added. After stirring for 2 h, the white precipitate was filtered and washed with MeOH and Et_2O. The resulting product was soluble in CH_3CN and H_2O. Complete substitution of the Cl^- by PF_6^- was confirmed by a qualitative test (no white precipitate was formed on addition of either Tl^+ or Ag^+ ions to a water solution of the product). In addition, scanning electron microscopy tests conducted on crystals of **1** showed no chloride Kα lines. Melting point = 205 °C. $^{31}P\{^1H\}$ NMR: (D_2O/H_2O, H_3PO_4) −60.3 ppm (broad), 78 ppm (PF_6^-). Anal. Calcd for $C_{26}H_{62}N_{13}O_4F_{24}P_8Au$: C, 20.50; H, 4.11; N, 11.97. Found: C, 19.42; H, 3.74; N, 10.95.

$[(TPA)_4Au](PF_6)\cdot 1.5HCl\cdot H_2O$, 2. Compound **2** was synthesized using the same procedure as in **1**. Partial substitution of the Cl^- anion in $[(HTPA)_3(TPA)Au]Cl_4\cdot 4H_2O$ with 1 equiv of $NaPF_6$ provided compound **2**.

$[(TPA)_4Au]Cl\cdot 6H_2O$, 3. $(Me_2S)AuCl$ (0.05 g, 0.17 mmol) was stirred in 10 mL of CH_2Cl_2/H_2O solvent mixture (1:1). The pH of the water had previously been adjusted to a pH = 10 by the addition of KOH. Four equivalents of the unprotonated TPA ligand were added (0.107 g, 6.69×10^{-4} mol), and the reaction mixture was stirred for 2 h. After the reaction was complete, the solvents were removed under reduced pressure and the residue was washed 4 × 5 mL with THF. The white product was then recrystallized from water. Yield = 65% based on Au. ^1H NMR: 4.88 ppm (d, 6H), 3.52 ppm (s, 6H). $^{31}P\{^1H\}$ NMR = −58 ppm (broad).

$[(MeTPA)_4Au](PF_6)_5\cdot 2CH_3CN$, 4. $(Me_2S)AuCl$ (42.7 mg, 0.145 mmol) was stirred with 4 equiv of $[MeTPA]PF_6$ (0.184 g, 5.80×10^{-4} mol) in 20 mL of CH_2Cl_2/H_2O solvent mixture (1:1). After the reaction was complete, the solvents were removed under reduced pressure, and the white residue was recrystallized from water. Yield = 71% based on Au. $^{31}P\{^1H\}$ NMR: −25.5 ppm, 83.0 ppm (PF_6^-).

Structural Results

Compounds **1**−**3** were all crystallized from H_2O, and compound **4** was crystallized from CH_3CN/Et_2O. Single crystals of each compound were mounted on glass fibers with epoxy resin, and data were collected. The details of the data collection and the refinement procedures have been published.[12] No decay was observed for the chosen standard reflections, ψ scans were used to correct for absorption as noted in Table 1. All the crystallographic data are contained in Table 1. The data have been corrected for decay and for Lorentz and polarization effects. Heavy atom positions were determined from direct methods and used as the initial phasing model for difference Fourier synthesis. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed to the carbon atoms in idealized positions at a distance of 0.96 Å.

The thermal ellipsoid plot of the structure of the cationic portion of $[(HTPA)_3(TPA)Au](PF_6)_4\cdot 4H_2O\cdot CH_3CN$ (**1**) is shown in Figure 1. Atomic coordinates are given in Table 2, and selected bond distances and angles are given in Table 3. The central gold atom is coordinated by four P atoms in a nearly tetrahedral geometry, where the six tetrahedral angles range from 106.8° to 111.3° with an average value of 109.5°. The Au−P distances range from 2.397 to 2.413 Å, distances which are somewhat shorter than the Au−P distances in $[Au(PPh_2Me)_4](BPh_4)$ as determined by Elder (2.449(1) Å).[7] The average P−C distance in **1**, 1.843 Å, is nearly identical to the distance found

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Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for $[(HPTA)_3(PTA)Au][PF_6]_4\cdot 4H_2O\cdot CH_3CN$ (**1**)

	x	*y*	*z*	*U*(eq)
Au	2454(1)	656(1)	7517(1)	23(1)
P(1)	2893(1)	678(2)	8993(1)	26(1)
P(2)	3469(1)	723(2)	7185(1)	26(1)
P(3)	1705(1)	1871(2)	6955(1)	26(1)
P(4)	1771(1)	−616(2)	6967(1)	26(1)
P(5)	4024(1)	6901(2)	3745(2)	36(1)
P(6)	3848(1)	1618(2)	3559(2)	41(1)
P(7)	352(1)	4397(2)	3340(2)	38(1)
P(8)	1641(1)	571(2)	4406(2)	44(1)
F(1)	4334(6)	1780(7)	3094(7)	146(7)
F(2)	3335(5)	1428(7)	3953(7)	163(8)
F(3)	3428(3)	2476(4)	3179(4)	73(3)
F(4)	4278(4)	773(4)	3936(4)	79(3)
F(5)	4351(6)	2119(6)	4267(6)	174(6)
F(6)	3365(6)	1122(6)	2783(6)	164(6)
F(7)	4482(4)	6398(5)	4545(5)	112(4)
F(8)	4405(3)	7782(4)	4100(4)	66(3)
F(9)	3573(4)	7375(5)	2920(5)	99(4)
F(10)	4582(4)	6691(5)	3380(6)	105(5)
F(11)	3463(4)	7088(5)	4091(6)	114(5)
F(12)	3624(3)	6023(4)	3373(4)	64(3)
F(13)	−216(4)	4321(5)	3713(5)	93(4)
F(14)	790(4)	5062(5)	4034(4)	95(4)
F(15)	−64(4)	5173(4)	2779(4)	82(4)
F(16)	−64(4)	3742(5)	2642(5)	90(4)
F(17)	783(4)	3623(5)	3895(5)	94(4)
F(18)	937(3)	4467(4)	2983(4)	72(3)
F(19)	1101(5)	1295(6)	3980(6)	130(6)
F(20)	2246(5)	1206(8)	4552(5)	153(6)
F(21)	1665(5)	766(5)	5275(4)	94(4)
F(22)	1625(4)	372(5)	3525(4)	87(4)
F(23)	1027(6)	−64(7)	4243(5)	149(6)
F(24)	2176(6)	−161(7)	4775(5)	165(7)
N(1)	2850(4)	−213(5)	10325(4)	29(3)
N(2)	3953(4)	518(5)	10544(4)	33(3)
N(3)	2915(4)	1354(5)	10439(4)	32(3)
N(4)	4917(4)	782(5)	7654(4)	35(3)
N(5)	4248(4)	−47(5)	6420(4)	33(3)
N(6)	4202(4)	1502(5)	6383(5)	40(4)
N(7)	405(4)	2563(5)	6011(5)	34(3)
N(8)	1088(4)	3336(5)	7269(4)	33(3)
N(9)	1422(4)	3405(5)	6110(5)	35(3)
N(10)	1208(4)	−2113(5)	7261(5)	36(3)
N(11)	561(4)	−1434(5)	5944(4)	34(3)
N(12)	1666(4)	−2175(5)	6187(5)	35(3)
C(1)	2578(5)	−236(6)	9401(5)	30(4)
C(2)	3844(4)	605(6)	9672(5)	32(4)
C(3)	2662(5)	1531(6)	9548(5)	35(4)
C(4)	2603(5)	585(6)	10598(6)	38(4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] Estimated standard deviations are given in parentheses.

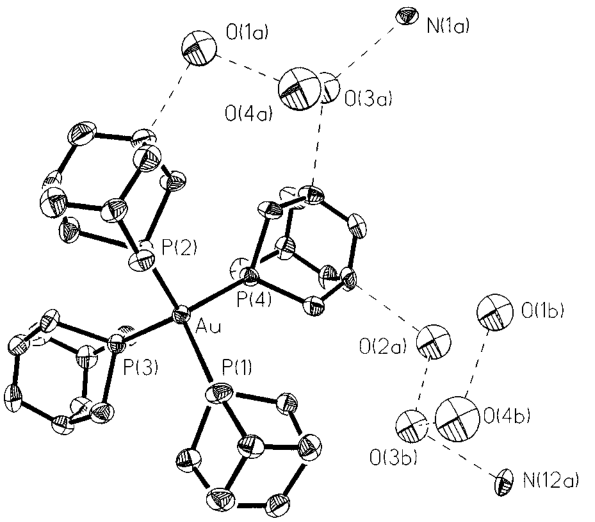

Figure 1. Partial thermal ellipsoid plot (50% probability) of **1**.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for $[(HTPA)_3(TPA)Au](PF_6)_4\cdot 4H_2O\cdot CH_3CN$ (**1**)

Au(1)−P(1)	2.413(2)	P(1)−Au(1)−P(2)	106.8(1)
Au(1)−P(2)	2.405(3)	P(1)−Au(1)−P(3)	109.8(1)
Au(1)−P(3)	2.397(2)	P(1)−Au(1)−P(4)	110.9(1)
Au(1)−P(4)	2.405(2)	P(2)−Au(1)−P(3)	110.2(1)
		P(2)−Au(1)−P(4)	111.3(1)
		P(3)−Au(1)−P(4)	108.0(1)

for the free TPA ligand.[13] Three of the four TPA ligands in **1** are protonated at N1, N5, and N8, thus giving a net +4 charge to the cation portion of the complex. The N−C distances for these quaternized N atoms are ca. 0.07 Å longer than the N-C bond distances of the tertiary N atoms. The average N−C distance for the quaternized N atoms is 1.52 Å. The structure contains four PF_6^- anions per Au atom.

Compound **1** crystallizes from an aqueous solution in a three-dimensional H-bonded network with $N{-}H^+\cdots OH_2$ and $HO{-}H\cdots OH_2$, as shown in Figure 1. The dominant intramolecular interaction in the structure is H-bonding between the four water molecules and the TPA ligands. The O···O distances between water molecules ranges from 2.679 to 2.856 Å, distances which are comparable to the O···O distances, 2.75−2.793 Å, found in ice,[14] thereby indicating strong H-bonding interactions.

The thermal ellipsoid plot of the structure of cationic portion of $[(TPA)_4Au](PF_6)\cdot 1.5HCl\cdot H_2O$ (**2**) is shown in Figure 2. Atomic coordinates are given in Table 4, and selected bond distances and angles are given in Table 5. As in complex **1**, the gold atoms are nearly tetrahedrally coordinated, with Au−P distances ranging from 2.371 to 2.395 Å and with P−Au−P angles which range from 104.5° to 113.4° (ave = 109.4°). One PF_6^- and 1.5 Cl^- anions per cation were found in the asymmetric unit along with two molecules of water.

An interesting feature found in the structure of **2** is the $N{-}H^+\cdots N$ interactions between six of the TPA ligands of the cation, as seen in Figure 2. The N−N distances range between 2.738 and 2.808 Å and indicate that the aggregation has been directed by the formation of hydrogen bonds between the two tetraphosphine coordinated Au centers. As a consequence, a layered supramolecular assembly is evident along the *b* axis of the crystal (figure in supporting information).

Unfortunately, the refinement for the four-coordinate Au(I) complex $[(TPA)_4Au]Cl\cdot 6H_2O$ (**3**) did not prove to be completely satisfactory. In the cubic space group $Fd\bar{3}m$, the gold atom occupies a special position which imposes a perfect tetrahedral geometry on the tetracoordinated cation. However, in this space group there are 421 out of 6175 reflections with a systematic absence violation for the data not corrected for absorption. Switching to the space group *Fd*3 (No. 203) or to the orthorhombic *Fddd* (No. 70) did not improve matters. Transformation to a lower symmetry orthorhombic cell or to a monoclinic cell eliminates the violations but doubles the volume. High correlations prevent refinement in such a supercell,

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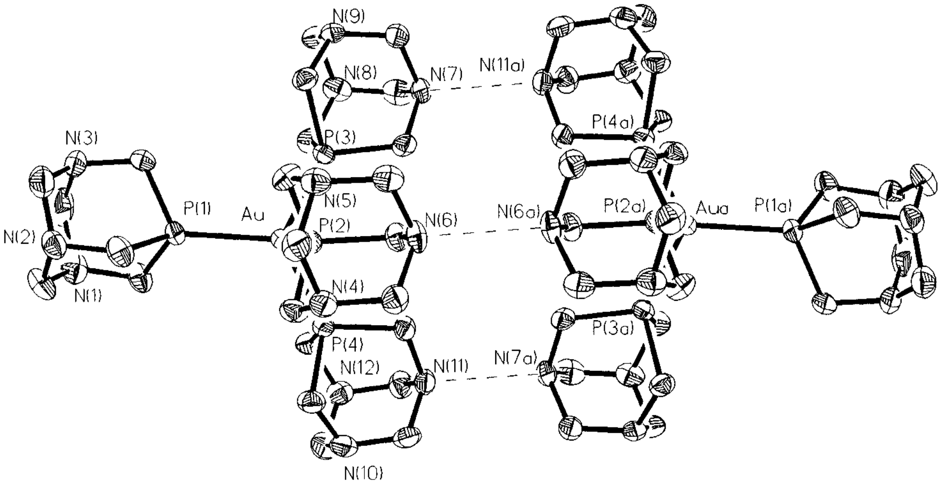

Figure 2. Partial thermal ellipsoid plot (50% probability) of **2**.

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $[(TPA)_4Au]PF_6 \cdot 1.5HCl \cdot H_2O$ (**2**)

	x	*y*	*z*	*U*(eq)		*x*	*y*	*z*	*U*(eq)
Au	3350(1)	1561(1)	2039(1)	26(1)	C(1)	2311(4)	435(8)	2044(4)	37(8)
Cl(1)	5000	8296(3)	2500	51(3)	C(2)	1733(4)	1154(9)	857(4)	43(8)
Cl(2)	4100(1)	3216(2)	997(1)	60(3)	C(3)	2163(4)	2861(8)	1761(4)	38(9)
P(1)	2425(1)	1491(2)	1694(1)	26(2)	C(4)	1119(4)	2363(9)	856(4)	46(9)
P(2)	3676(1)	3557(2)	2159(1)	26(2)	C(6)	1615(4)	1738(8)	1865(4)	42(9)
P(4)	4159(1)	669(2)	3044(1)	27(2)	C(5)	1240(4)	289(9)	1090(5)	54(10)
P(3)	3201(1)	583(2)	1256(1)	25(2)	C(7)	3926(4)	4573(7)	2777(4)	32(7)
P(5)	1766(1)	6691(3)	1069(1)	47(2)	C(8)	3196(3)	4614(7)	1500(4)	34(7)
F(1)	1761(3)	6208(7)	596(3)	100(8)	C(9)	4341(3)	3664(7)	2332(4)	31(7)
F(2)	1768(3)	7174(6)	1546(3)	74(6)	C(10)	3680(4)	6367(7)	2181(4)	38(8)
F(3)	1198(3)	7485(7)	533(3)	115(8)	C(12)	4018(4)	5583(8)	1783(4)	34(7)
F(4)	2325(3)	5860(6)	1609(3)	73(6)	C(11)	4663(3)	5568(8)	2907(4)	34(7)
F(5)	2207(4)	7714(7)	1292(4)	109(10)	C(17)	3835(3)	450(7)	1379(3)	29(7)
F(6)	1323(3)	5641(6)	864(3)	97(7)	C(18)	3422(4)	−1400(8)	741(4)	42(8)
N(1)	1707(3)	542(7)	1767(4)	42(7)	C(15)	2948(4)	−975(8)	1033(4)	38(8)
N(2)	1579(3)	2680(7)	1519(3)	37(7)	C(16)	3171(3)	542(8)	233(4)	36(7)
N(3)	1193(3)	1191(7)	714(3)	42(6)	C(13)	2660(4)	1230(7)	461(4)	33(7)
N(4)	4148(3)	5717(6)	2778(3)	33(6)	C(19)	4479(4)	1380(8)	3768(4)	37(7)
N(5)	3494(3)	5741(6)	1642(3)	35(6)	C(23)	5485(4)	648(8)	4415(4)	39(7)
N(6)	4510(3)	4932(6)	2382(3)	31(6)	C(21)	4862(3)	485(8)	3288(3)	31(7)
N(7)	3657(3)	−160(6)	837(3)	34(6)	C(20)	4098(4)	−847(7)	3203(4)	33(7)
N(8)	2862(3)	−1390(6)	535(3)	37(6)	C(22)	4820(4)	−510(8)	4325(4)	42(8)
N(9)	2606(3)	531(6)	30(3)	29(5)	C(14)	2418(4)	−691(8)	−40(4)	40(8)
N(10)	4993(3)	707(6)	4331(3)	37(6)	C(24)	5150(4)	−1310(8)	3919(4)	39(8)
N(11)	5335(3)	−100(6)	3916(3)	33(6)	O(1)	263(4)	883(12)	−652(4)	159(10)
N(12)	4653(3)	−1266(6)	3834(3)	37(6)	O(2)	1149(5)	−1101(9)	−399(5)	137(15)

Table 5. Selected Interatomic Distances (Å) and Angles (deg) for $[(TPA)_4.Au]PF_6 \cdot 1.5HCl \cdot H_2O$ (**2**)

Au(1)−P(1)	2.371(2)	P(1)−Au(1)−P(2)	112.4(1)
Au(1)−P(2)	2.390(3)	P(1)−Au(1)−P(3)	107.3(1)
Au(1)−P(3)	2.395(2)	P(1)−Au(1)−P(4)	110.9(1)
Au(1)−P(4)	2.383(2)	P(2)−Au(1)−P(3)	110.2(1)
		P(2)−Au(1)−P(4)	111.3(1)
		P(3)−Au(1)−P(4)	108.0(1)

however. It appears that the failure of $Fd\bar{3}m$ is largely a result of misalignment of the water and chlorine atoms, although thermal parameters appear normal. Consequently, although the geometry about the gold atom must not be rigorously tetrahedral (by crystallographic symmetry), the near tetrahedral structure so dominates the scattering that lower symmetry refinement is not viewed by us to be cost effective. A thermal ellipsoid drawing of the structure of **3** is shown in Figure 3. Atomic coordinates are given in Table 6, and selected bond distances and angles are given in Table 7. None of the four TPA ligands are protonated, although weak H-bonding to the water molecule occurs for one of these N atoms. There is only one chloride anion per $[(TPA)_4Au]^+$ cation in the asymmetric unit. The Au−P bond length is 2.385(5) Å, which is in the range observed for all of the four-coordinate complexes, and the C−N distance is normal, 1.45(2) Å, for the nonprotonated N atoms. The lattice contains six molecules of water for each cation, and the water

Table 6. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $[(TPA)_4Au]Cl \cdot 6H_2O$ (**3**)

	x	*y*	*z*	*U*(eq)
Au(1)	1250	1250	1250	28(1)
Cl(1)	3750	3750	3750	43(2)
P(1)	1938(1)	1938(1)	1938(1)	31(1)
N(1)	2919(3)	2919(3)	2033(5)	38(2)
X(1)	2524(4)	2524(4)	1570(6)	34(2)
C(2)	2470(4)	2470(4)	3317(6)	34(2)
O(1)	3750	1274(4)	3750	14(2)

Table 7. Selected Interatomic Distances (Å) and Angles (deg) for $[(TPA)_4Au]Cl \cdot 6H_2O$ (**3**)

Au(1)−P(1)	2.385(5)	P(1)−Au(1)−P(2)	109.5
P(1)−C(1)	1.81(1)		
N(1)−C(1)	1.45(2)		
O(1)···N(1)	2.799		

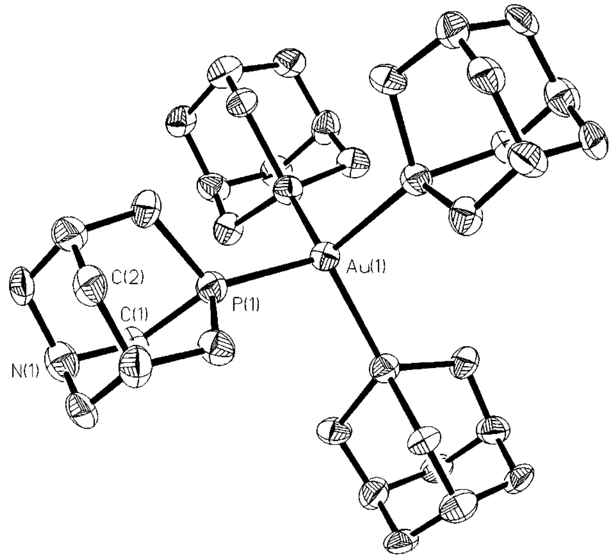

Figure 3. Partial thermal ellipsoid plot (50% probability) of **3**.

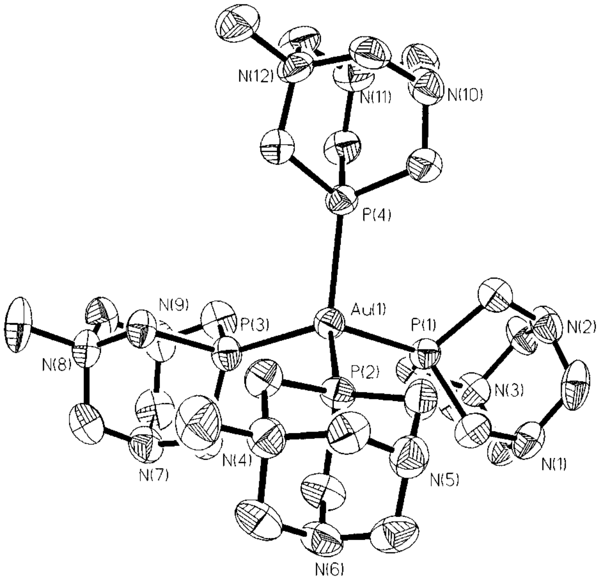

Figure 4. Partial thermal ellipsoid plot (50% probability) of **4**.

molecules hydrogen bond to one of the nitrogen atoms of the TPA ligand with an O···N distance of 2.8 Å.

The cation portion of the methylated complex $[(MeTPA)_4Au](PF_6)_5 \cdot 2CH_3CN$ (**4**) is shown in the thermal ellipsoid plot, Figure 4. Atomic coordinates are given in Table 8, and selected bond distances and angles are given in Table 9. The central gold atom is coordinated to four TPA ligands that are all methylated at one of the nitrogen centers (N3, N4, N8, N12), forming an almost regular tetrahedron. The tetrahedral angles are in the range 104.10−113.88° (ave = 109.4°) and the Au−P distances are in the range 2.398−2.423 Å. As in the protonated ligand, the C−N distances to the quaternized nitrogens are on average significantly longer than the distances to the tertiary nitrogens (ave = 1.52 Å for the quaternized nitrogens compared to 1.45 Å for the tertiary nitrogens). The N−C distances of the quaternized N atoms range from 1.485 to 1.501 Å, the usual distance found for a N−C single bond. The cation has a +5 charge, and as expected, five PF_6^- anions are found in the asymmetric unit. Two acetonitrile solvent molecules are also found in the asymmetric unit.

Discussion

Four different four-coordinate Au(I) complexes with the monodentate phosphine TPA have been synthesized and structurally characterized. All of them show a nearly regular tetrahedral AuP_4 geometry at the gold center with average tetrahedral angles close to 109.5°. As was mentioned previously, four-coordination for gold(I) has often been observed, but few examples have been confirmed crystallographically.[2,3] Although it has been shown that the steric bulk of the ligand is important,[15] the ability of the TPA ligand to form strong hydrogen bonds in water must also be a factor in the ease of isolation of these complexes. Ligands with a similar cone angle to TPA, such as PMe_3 or PEt_3, tend to crystallize[15] as linear [LAuX], X = halide, or $[AuL_2]^+X$ complexes although three- and four-coordinate species also can be formed.[1]

Complexes **1** and **2** are interesting because during the isolation of the crystals at least one of the ligands has lost a proton. The syntheses started with the protonated ligand and a gold(I) starting material. Attempts to crystallize a four-coordinate complex containing four protonated TPA ligands failed, even when the reaction and the crystallization were performed in 1.5 M HCl. The counterions obviously play a role in determining the extent of protonation of the ligands and the nature of the intermolecular hydrogen-bonding interactions. Complete substitution of the Cl^- by PF_6^- as in **1** gives a three-dimensional hydrogen-bonded network involving three protonated nitrogen centers with water molecules in the lattice. The protonated N atoms are H-bonded to H_2O molecules and show a fairly short $N-H^+ \cdots O$ separation that ranges from 2.687 to 2.88 Å. Crystals of **1** are robust and do not appear to lose H_2O prior to decompostion at 205 °C. Attempts to obtain a crystalline product from organic solvents such as CH_3CN or MeOH failed, indicating that the participation of the H_2O molecules in hydrogen bonding to the Au(I) cation is important in sustaining the stability and crystallinity of the complex.

Partial replacement of the Cl^- ions with PF_6^- led to the isolation of complex **2**, which shows only 1.5 protonated nitrogen centers for each cation. This is especially unusual because it produces an example of a supramolecular assembly directed by the formation of hydrogen bonds between neighboring cations. Molecular recognition between a R_3NH^+ unit of one cation which acts as a proton donor and a coordinated TPA on another gold atom which acts as a proton acceptor dictates the hydrogen-bonding interactions observed in **2.** Whereas, in **1**, the H-bonding to the Au(I) cations involves lattice water and Cl^-, not other TPA ligands, a layered assembly for **2** is observed. The formation of supramolecular assemblies directed by molecular recognition is frequently observed in organic and bioorganic systems where the assembly is held together by strong hydrogen-bonding interactions such as $N-H \cdots O$ and $O-H \cdots O$, as well as by weaker $C-H \cdots O$ interactions.[16] Controlling the formation of these assemblies is of considerable importance.[17]

The formation of a four-coordinate complex containing four unprotonated TPA ligands was achieved by performing the reaction in a basic solution at pH = 10. Complex **3** crystallizes with each Au(I) atom in what appears to be a nearly perfect

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Table 8. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $[(TPA)_4Au](PF_6)_5 \cdot 2CH_3CN$ (**4**)

	x	*y*	*z*	*U*(eq)		*x*	*y*	*z*	*U*(eq)
Au(1)	2839(1)	2693(1)	1626(1)	38(1)	P(7)	4706(1)	3839(2)	666(1)	62(1)
P(1)	2974(1)	2878(2)	2312(1)	37(1)	P(8)	2370(1)	8735(2)	711(1)	59(1)
P(2)	1882(1)	2064(2)	1448(1)	39(1)	P(9)	5000	4374(3)	2500	67(1)
P(3)	3537(1)	1652(2)	1443(1)	41(1)	P(10)	1141(1)	4697(2)	2265(1)	50(1)
P(4)	2949(1)	4187(2)	1385(1)	40(1)	F(1)	3142(9)	2199(14)	−31(6)	120(6)
N(1)	2583(3)	2484(6)	2992(2)	51(2)	F(1B)	2589(11)	2284(16)	−428(7)	128(9)
N(2)	2981(4)	3982(5)	2937(2)	54(2)	F(2)	2396(7)	1507(10)	123(4)	84(4)
N(3)	3625(4)	2670(5)	3031(2)	48(2)	F(2B)	2701(11)	1508(17)	36(17)	146(8)
N(4)	1075(3)	1377(5)	860(2)	47(2)	F(3)	2632(6)	2551(9)	457(4)	54(3)
N(5)	707(3)	1934(6)	1432(2)	52(2)	F(3B)	3132(8)	2843(12)	107(5)	104(5)
N(6)	1231(3)	522(5)	1463(2)	51(2)	F(7)	412(3)	5051(5)	385(2)	96(2)
N(7)	4018(4)	−31(5)	1455(2)	56(2)	F(8)	460(3)	4242(4)	927(2)	77(2)
N(8)	4065(3)	826(5)	870(2)	48(2)	F(9)	1030(3)	5461(5)	904(2)	80(2)
N(9)	4687(3)	1224(6)	1474(2)	54(2)	F(10)	1371(3)	4874(4)	390(2)	73(2)
N(10)	2555(3)	5931(5)	1351(2)	48(2)	F(11)	1416(3)	4067(4)	934(2)	74(2)
N(11)	3591(3)	5726(5)	1352(2)	54(2)	F(12)	807(3)	3658(5)	419(2)	81(2)
N(12)	2922(3)	5372(5)	776(2)	45(2)	F(13)	5151(4)	4195(6)	409(2)	106(2)
C(1)	2468(4)	2293(7)	2574(3)	49(2)	F(14)	5195(4)	3369(6)	945(2)	107(2)
C(2)	2932(4)	4016(6)	2515(2)	46(2)	F(15)	4188(3)	4301(5)	396(2)	94(2)
C(3)	3648(4)	2519(6)	2605(3)	41(2)	F(16)	4232(3)	3489(5)	926(2)	94(2)
C(4)	2513(4)	3443(4)	3062(3)	62(3)	F(17)	4773(3)	4733(5)	923(2)	79(2)
C(5)	3535(4)	3680(6)	3107(3)	53(2)	F(18)	4615(3)	2952(5)	418(2)	89(2)
C(6)	3130(4)	2165(7)	3162(3)	49(2)	F(19)	1930(4)	8293(6)	961(2)	115(3)
C(7)	4191(5)	2367(8)	3249(3)	69(3)	F(20)	2311(4)	7911(6)	429(2)	107(3)
C(8)	1800(4)	903(6)	1608(3)	51(2)	F(21)	2894(3)	8280(5)	978(2)	92(2)
C(9)	1648(4)	1878(7)	936(2)	46(2)	F(22)	2814(3)	9188(5)	465(2)	90(2)
C(10)	1198(4)	2519(6)	1576(3)	48(2)	F(23)	1848(3)	9216(5)	453(2)	83(2)
C(11)	766(4)	1043(7)	1592(3)	56(3)	F(24)	2436(3)	9579(5)	992(2)	100(2)
C(12)	1137(4)	462(6)	1058(3)	57(3)	F(25)	5048(10)	4679(18)	2106(6)	139(7)
C(13)	608(4)	1909(7)	1031(3)	48(2)	F(25B)	5079(7)	4043(13)	2063(5)	106(5)
C(14)	912(5)	1256(8)	442(3)	68(3)	F(26)	5035(9)	3308(9)	2605(4)	100(5)
C(15)	4308(4)	1903(7)	1603(3)	55(2)	F(27)	4312(6)	4499(10)	2484(4)	69(4)
C(16)	3538(4)	461(6)	1587(3)	52(2)	F(27B)	4963(7)	5351(12)	2315(4)	107(5)
C(17)	3581(4)	1469(6)	936(2)	44(2)	F(28)	4326(6)	4237(10)	2344(4)	67(4)
C(18)	4645(4)	1196(7)	1065(3)	55(3)	F(31)	1131(3)	5183(5)	1865(2)	80(2)
C(19)	3973(4)	−79(7)	1052(3)	58(3)	F(32)	1174(3)	4223(5)	2665(2)	82(2)
C(20)	4590(5)	328(7)	1621(3)	62(3)	F(33)	1594(3)	3982(4)	2144(2)	75(2)
C(21)	4077(5)	739(9)	448(3)	74(3)	F(34)	619(3)	4076(4)	2093(2)	77(2)
C(22)	2442(4)	5055(6)	1512(3)	48(2)	F(35)	716(3)	5437(5)	2392(2)	80(2)
C(23)	2859(4)	4398(6)	868(2)	45(2)	F(36)	1683(3)	5326(4)	2439(2)	67(2)
C(24)	3632(4)	4812(6)	1515(3)	51(2)	N(1S)	3917(5)	6780(9)	2419(4)	102(4)
C(25)	3142(5)	6256(6)	1495(3)	58(3)	C(1S)	4167(6)	7113(10)	2227(4)	89(4)
C(26)	2472(5)	5935(6)	942(3)	54(2)	C(2S)	4506(10)	7505(13)	1964(6)	149(8)
C(27)	3517(4)	5731(7)	945(3)	57(3)	N(2S)	4244(10)	7576(13)	651(7)	174(8)
C(28)	2845(5)	5487(7)	349(3)	65(3)	C(3S)	4195(10)	7639(14)	313(7)	136(7)
P(5)	3500	2500	0.0000	45(1)	C(4S)	4112(10)	7854(16)	−83(6)	174(9)
P(6)	906(1)	4562(2)	657(1)	54(1)					

Table 9. Selected Interatomic Distances (Å) and Angles (deg) for $[(TPA)_4Au](PF_6)_5 \cdot 2CH_3CN$ (**4**)

Au(1)−P(1)	2.416(2)	P(1)−Au(1)−P(2)	106.87(8)
Au(1)−P(2)	2.423(2)	P(1)−Au(1)−P(3)	110.17(8)
Au(1)−P(3)	2.398(2)	P(1)−Au(1)−P(4)	104.10(7)
Au(1)−P(4)	2.403(2)	P(2)−Au(1)−P(3)	108.53(8)
		P(2)−Au(1)−P(4)	113.88(8)
		P(3)−Au(1)−P(4)	113.02(8)

AuP_4 tetrahedron. (Such a geometry is dictated by the space group chosen for refinement. However, as stated above, there are problems with this interpretation of the data.) The lack of protonation is confirmed by the location of only one anion in the lattice. The ^1H NMR shows a singlet at 3.52 ppm and a doublet at 4.88 ppm assigned to the nitrogen-bound methylene hydrogen atoms and the phosphorus-bound methylene hydrogen atoms, respectively. Figure 5 shows the packing diagram for the complex and illustrates how the water molecules are involved in a regular three-dimensional packing arrangement. There are six water molecules for every $[(TPA)_4Au]^+$ cation, and all 12 nitrogen atoms of the TPA appear to hydrogen bond to a water molecule in the lattice. This may be the origin of the pseudosymmetry since it is unlikely that each water H atom is H-bonded equivalently to two TPA ligands. However, the crystallographic disorder implied could not be detected. The packing does suggest that the ability of the TPA ligand to hydrogen bond to water plays an important role in promoting the formation and organization of the four-coordinate species.

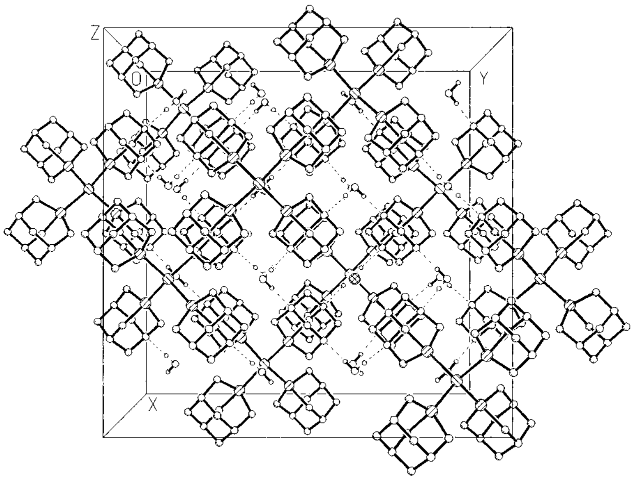

Figure 5. Packing diagram for **3**.

In our studies of the coordination[18] of TPA to gold(I), it frequently has been found that attempts to crystallize the three-coordinate cation $[L_3Au]^+$ lead to the isolation of the $[L_4Au]^+$ species. The tetrahedral geometry of the four-coordinate cations leads to the formation of stable crystalline products from water.

Although the $[(HTPA)_4Au]^{5+}$ could not be isolated in our hands, the analogue $[(MeTPA)_4Au]^{5+}$ (**4**) has been structurally characterized. Each of the four TPA ligands are methylated at one of the nitrogen atom centers. Five PF_6^- anions are found in the asymmetric unit. This complex is less soluble in water than either the protonated or unprotonated complexes, but it can be crystallized from either water or acetonitrile. The cation also shows a nearly regular tetrahedral geometry at the gold center.

Conclusion

Utilization of the small cone angle of TPA (102°) and its ability to form hydrogen-bonding interactions in aqueous solution have led to the formation of a series of four-coordinate, tetrahedral gold(I) complexes. In **2**, where an $N^+H\cdots N$ interaction is present between two neighboring groups, molecular recognition of the hydrogen bonds leads to aggregation and a supramolecular assembly.

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Supporting Information Available: Tables of data collection information, anisotropic thermal parameters, hydrogen atom coordinates, bond lengths and angles, and figures for **1**−**4** are available (65 pages). Ordering information is given on any current masthead page.

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