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Gold(I)−Purine Interactions: Synthesis and Characterization of Cyclic and Open Chain Polynuclear Gold(I) Complexes Containing Xanthine Derivatives and Bis(phosphine) as Bridging Ligands. Crystal Structures of $[Au_2(\mu\text{-HX})(\mu\text{-dmpe})]\cdot 3H_2O$ and $[Au_2(\mu\text{-TT})(\mu\text{-dmpe})]\cdot H_2O$ (H_3X = Xanthine; H_2TT = 8-Mercaptotheophylline)

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The reaction of $[(AuBr)_2(\mu\text{-}PR_2P(CH_2)_nPR_2)]$ (where R = CH_3 for n = 1; R = Ph for n = 1, 3, 4) with *N*-alkylxanthine and thioxanthine derivatives, containing two ionizable protons in close positions, yields, under basic conditions, neutral heterobridged dinuclear gold(I) ring complexes $[Au(\mu\text{-L})_2(\mu\text{-}PR_2P(CH_2)_nPR_2)]$, which have been investigated by means of ^{1}H- and ^{31}P-NMR and FAB spectroscopies. Crystal structures of two of these complexes are reported. $[Au_2(\mu\text{-HX})(\mu\text{-dmpe})]\cdot 3H_2O$ **(1)** (H_3X = xanthine; dmpe = 1,2-bis(dimethylphosphine)ethane) crystallizes in the monoclinic space group $P2_1/n$ with a = 9.348(2) Å, b = 8.656(2) Å, c = 24.585(5) Å, β = 98.24(2)°, Z = 4, and R = 0.040. $[Au_2(\mu\text{-TT})(\mu\text{-dmpe})]\cdot H_2O$ **(2)** crystallizes in the monoclinic space group $P2_1/n$ with a = 10.853(4) Å, b = 14.031(6) Å, c = 13.574(5) Å, β = 100.80(4)°, Z = 4, and R = 0.063. The structures of **1** and **2** are similar and consist of dinuclear nine-membered ring molecules, in which the two linear two-coordinate gold atoms are bridged on one side by a dmpe ligand and on the other side by a bidentate xanthinato dianion, with intramolecular Au···Au distances of 3.053(1) and 2.952 (2) Å, respectively. In the former, the coordination of the xanthinato ligand to the gold atoms takes place through the N3 and N9 nitrogen atoms whereas, in the latter, N7,S8-chelate coordination of the 8-thiotheophyllinato dianion occurs. The magnitude of the Au···Au separation is analyzed in terms of the twisting of the xanthine derivative ligand from the plane containing the gold(I) and phosphorus atoms. For n = 6 the steric requirements of the Au(μ-dpph)Au group prevents the formation of dinuclear ring complexes and open chain complexes are obtained. Finally, when the xanthine derivatives do not contain two close active coordination sites dinuclear open chain complexes are formed.

Introduction

Gold coordination chemistry has received much attention in recent years, mainly due to (i) the weak metal−metal interactions observed in gold(I) complexes,[1,2] which have been attributed to relativistic effects,[3] (ii) the rich photophysical and photochemical properties that exhibit polynuclear gold(I) complexes, particularly those containing phosphine bridging ligands,[4−6] which seem to be related to the Au···Au separation, and (iii) the successful use of gold(I)−phosphine complexes as antiarthritis drugs and antitumor agents.[7−9]

We have previously investigated the interaction of chloro(triphenylphosphine)gold(I) and [μ-1,2-bis(diphenylphosphine)ethane]bis[bromogold(I)] with oxo- and oxothiopurines[10] and found that some of the isolated (purine)gold(I) phosphine complexes display a high degree of cytotoxic activity in vitro.[11] It was noteworthy that 8-thiopurines containing two ionizable protons in close positions, such as 8-thiotheophylline, react with $[(AuBr)_2(\mu\text{-dppe})$ to afford dinuclear gold(I) ring complexes.[10b] Although no single crystals of these compounds suitable for X-ray diffraction analysis were obtained, the spectroscopic data clearly suggested S7,N8-chelate coordination of the ligands in these complexes. It should be noted that the majority of dinuclear gold(I) ring compounds are homobridged complexes with the same bridging ligand of each side[12] but only a few examples of heterobridged complexes have been reported so far.[13]

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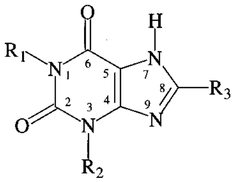
Chart 1



H_3X	Xanthine $R_1 = R_2 = R_3 = H$
H_2TT	1,3-Dimethyl-8-thioxanthine (8-Thiotheophylline) $R_1 = R_2 = CH_3$ $R_3 = SH$
H_2MX	1-Methyl-8-ethylxanthine $R_1 = CH_3$ $R_2 = H$ $R_3 = CH_2\text{-}CH_3$
H_2ME	3-Methyl-8-ethylxanthine $R_1 = H$ $R_2 = CH_3$ $R_3 = CH_2\text{-}CH_3$

Here we report the preparation and characterization of several heterobridged dinuclear gold(I) ring and open ring complexes obtained by interaction, under basic conditions, of xanthine and some of its alkyl and thio derivatives (Chart 1) with $[(AuBr)_2(\mu\text{-bis(phosphine)})]$ in which the number of methylene groups in the bridging bis(phosphine) backbone (*n*) is systematically varied from 1 to 6. The molecular structures of two heterobridged dinuclear gold(I) complexes, $[Au_2(\mu\text{-HX})(\mu\text{-dmpe})]\cdot 3H_2O$ **(1)** and $[Au_2(\mu\text{-TT})(\mu\text{-dmpe})]\cdot H_2O$ **(2)**, have been established by X-ray studies and show the existence of gold−gold interactions.

Experimental Section

All reactions were carried out by using standard inert-atmosphere techniques. Xanthine and bis(phosphines) were purchased from Aldrich and used as received. The purine derivatives 1,3-dimethyl-8-thioxanthine (8-thiotheophylline), 1-methyl-8-ethylxanthine and 3-methyl-8-ethylxanthine were prepared according to literature procedures.[14,15] Solvents were reagent grade and were used without further purification. The $[(AuBr)_2(\mu\text{-bis(phosphine)})]$ complexes were prepared as we previously described.[10] The following abbreviations for bis(phosphines) are used: dppm = 1,2-bis(diphenylphosphino)methane, dmpe = 1,2-bis(dimethylphosphino)ethane, dppp = 1,2-bis(diphenylphosphino)propane, dppb =1,2-bis(diphenylphosphino)butane, and dpph = 1,2-bis(diphenylphosphino)hexane.

Physical Measurements. Microanalyses and IR and ^1H- and $^{31}P\{^1H\}$-NMR spectra were obtained as already described.[10] The positive-ion fast atom bombardment (FAB) mass spectra were recorded on a VG Autospec mass spectrometer, using 3-nitrobenzyl alcohol as matrix.

Preparations. All complexes were prepared by following the same method: a suspension of $[(AuBr)_2(\mu\text{-bis(phosphine)})]$ (2 mmol in 50 mL of ethanol) was added to a solution of purine derivative (2 mmol in 5 mL of water) containing 2 mmol of KOH. The suspension was refluxed for 30 min until an almost clear solution was obtained. After filtration of any amount of insoluble material, the resulting colorless solution was allowed to stand at room temperature, whereupon white products formed (prismatic crystals in the case of the complexes **1**, **2**, and **3**).

$[Au_2(\mu\text{-HX})(\mu\text{-dmpe})]\cdot 3H_2O$ (1). Yield: 80%. Anal. Calcd for $C_{11}H_{24}N_4O_5P_2Au_2$: C, 17.66; H, 3.23; N, 7.49; Au, 52.65. Found: C, 17.68; H, 3.23; N, 7.50; Au, 52.65. IR (KBr, cm^{-1}): υ(N1−H) 2974; υ(C6═O) 1609; υ(C2═O) 1690. ^1H NMR in DMSO-d_6 (δ, ppm): 9.60 (s, 1H, N(1)H); 7.05 (s, 1H, C(8)H); 2.3−2.5 (m, 4H, PCH_2CH_2P); 1.84 (d, $^2J_{PH}$ = 11.3 Hz, 6H, $P(CH_3)_2$); 1.79 (d, $^2J_{PH}$ = 11.3 Hz, 6H, $P(CH_3)_2$).

$[Au_2(\mu\text{-TT})(\mu\text{-dmpe})]\cdot H_2O$ (2). Yield: 85%. Anal. Calcd for $C_{13}H_{24}N_4O_3P_2SAu_2$: C, 20.22; H, 3.13; N, 7.25; Au, 51.01. Found: C, 20.20; H, 3.31; N, 7.27; Au, 50.37. IR (KBr, cm^{-1}): υ(C6═O) 1676; υ(C2═O) 1616; ^1H NMR in DMSO-d_6 (δ, ppm): 3.31 (s, 3H, N(3)-CH_3); 3.14 (s, 3H, N(1)CH_3); 2.2−2.4 (m, 4H, PCH_2CH_2P); 1.69 (d, $^2J_{PH}$ = 11.2 Hz, 6H, $P(CH_3)_2$); 1.62 (d, $^2J_{PH}$ = 10.9 Hz, 6H, $P(CH_3)_2$).

$[Au_2(\mu\text{-MX})(\mu\text{-dmpe})]\cdot KBr\cdot 2H_2O$ (3). Yield: 60%. Anal. Calcd for $C_{14}H_{28}N_4O_4P_2KBrAu_2$: C, 18.87; H, 3.17; N 6.29; Au, 44.20. Found: C, 19.20; H, 3.35; N, 6.73; Au, 44.70. IR (KBr, cm^{-1}): υ(C6═O) 1659; υ(C2═O) 1600. ^1H NMR in DMSO-d_6 (δ, ppm): 3.11 (s, 3H, N(1)CH_3); 2.58 (q, J_{HH} = 7.5 Hz, 2H, C8−CH_2); 2.2−2.4 (m, 4H, PCH_2CH_2P); 1.72 (d, $^2J_{PH}$ = 11.4 Hz, 6H, $P(CH_3)_2$); 1.68 (d, $^2J_{PH}$ = 11.2 Hz, 6H, $P(CH_3)_2$); 1.23 (t, J_{HH} = 7.5 Hz, 3H, CH_3).

$[Au_2(\mu\text{-HX})(\mu\text{-dppp})]$ (4). Yield: 90%. Anal. Calcd for $C_{32}H_{28}N_4O_2P_2Au_2$: C, 40.18; H, 2.95; N, 5.86; Au, 41.19. Found: C, 40.26; H, 3.01; N, 5.90; Au, 41.57. IR (KBr, cm^{-1}): υ(N1−H) 2976; υ(C2═O) 1680; υ(C6═O) 1614.

$[Au_2(\mu\text{-HX})(\mu\text{-dppb})]\cdot H_2O$(5). Yield: 82%. Anal. Calcd for $C_{33}H_{32}N_4O_3P_2Au_2$: C, 40.10; H, 3.26; N, 5.67; Au, 39.85. Found: C, 40.47; H, 3.41; N, 5.58; Au, 40.07. IR (KBr, cm^{-1}): υ(N1−H) 2976; υ(C6═O) 1614; υ(C2═O) 1680.

$[Au_2(\mu\text{-TT})(\mu\text{-dppm})]$ (6). Yield: 84%. Anal. Calcd for $C_{32}H_{28}N_4O_2P_2SAu_2$: C, 38.88; H, 2.85; N, 5.67; Au, 39.85. Found: C, 39.05; H, 3.02; N, 5.63; Au, 39.70. IR (KBr, cm^{-1}): υ(C6═O) 1680; υ(C2═O) 1643. ^1H NMR in DMSO-d_6 (δ, ppm): 3.37 (s, 3H, N(3)-CH_3); 3.17 (s, 3H, N(1)CH_3); 7.3−8.3 (3m, 20H, PPh_2) 2.2−2.4 (m, 4H, PCH_2CH_2P).

$[Au_2(\mu\text{-TT})(\mu\text{-dppp})]\cdot H_2O$ (7). Yield: 87%. Anal. Calcd for $C_{34}H_{34}N_4O_3P_2SAu_2$: C, 39.47; H, 3.31; N, 5.42; Au, 38.08. Found: C, 39.45; H, 3.11; N, 5.45; Au, 38.65. IR (KBr, cm^{-1}): υ(C6═O) 1681; υ(C2═O) 1642.

$[Au_2(\mu\text{-TT})(\mu\text{-dppb})]$ (8). Yield: 77%. Anal. Calcd for $C_{35}H_{34}N_4O_2P_2SAu_2$: C, 40.79; H, 3.33; N, 5.44; Au, 38.22. Found: C, 40.62; H, 3.37; N, 5.37; Au, 38.51. IR (KBr, cm^{-1}): υ(C6═O) 1676; υ(C2═O) 1636.

$[Au_6(\mu\text{-X})(\mu\text{-dpph})_3Br_3]$ (9). Yield: 16%. Anal. Calcd for $C_{95}H_{97}N_4O_2P_6Au_6Br_3$: C, 38.89; H, 3.33; N, 1.91; Au, 40.28; Br, 8.17. Found: C, 38.61; H, 3.43; N, 1.91; Au, 40.29; Br, 7.85. IR (KBr, cm^{-1}): υ(C6═O) 1618; υ(C2═O) 1618.

$[Au_4(\mu\text{-TT})(\mu\text{-dpph})_2Br_2]$ (10). Yield: 25%. Anal. Calcd for $C_{67}H_{70}N_4O_2P_4SAu_4Br_2$: C, 38.93; H, 3.41; N, 2.71; Au, 38.12; Br, 7.73. Found: C, 39.07; H, 3.39; N, 2.75; Au, 38.32; Br, 6.91. IR (KBr, cm^{-1}): υ(C6═O) 1679; υ(C2═O) 1639.

$[Au_2(HME)_2(\mu\text{-dppb})]\cdot H_2O$ (11). Yield: 55%. Anal. Calcd for $C_{44}H_{46}N_8O_5P_2Au_2$: C, 43.22; H, 3.79; N, 9.16; Au, 32.22. Found: C, 40.84; H, 3.57; N, 8.82; Au, 33.72. IR (KBr, cm^{-1}): υ(N1−H) 3147; υ(C6═O) 1677; υ(C2═O) 1660; ^1H NMR in DMSO-d_6 (δ, ppm): 10.55 (s, 1H, N(1)H); 7.4−7.8 (2m, 20H, PPh_2) 3.32 (s, 3H, N(3)CH_3); 2.85 (broad singlet, 4H, PCH_2); 2.85 (q, J_{HH} = 7.5 Hz, 2H, C8−CH_2); 1.85 (broad singlet, 4H, CH_2−CH_2); 1.24 (t, J_{HH} = 7.5 Hz, 3H, CH_3).

X-ray Data Collections and Structure Determination of the Compounds. Single-crystal collections for **1** and **2** were performed at 295 K with a Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.710 69 Å). The unit cell parameters were calculated by least-squares refinement of 50 well-centered reflections for **1** (θ_{max} = 20°) and 25 for **2** ($14 < 2\theta < 22°$). The data were collected by a $\omega - 2\theta$ scan mode. Intensities of three reflections monitored periodically exhibited no significant variation. Data were corrected for Lorentz and polarization effects. An empirical

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Table 1. Crystal Data and Structure Determination Parameters for **1** and **2**

	$[Au_2(\mu\text{-dmpe})(\mu\text{-HX})]$ (**1**)	$[Au_2(\mu\text{-dmpe})(\mu\text{-TT})]$ (**2**)
formula	$Au_2C_{11}H_{18}N_4O_2P_2 \cdot 3H_2O$	$Au_2C_{13}H_{22}N_4O_2P_2S \cdot H_2O$
fw	748.22	772.30
space group, cryst syst	$P2_1/n$, monoclinic	$P2_1/n$, monoclinic
a, Å	9.348(2)	10.853(4)
b, Å	8.656(2)	14.031(6)
c, Å	24.585(5)	13.574(5)
α, deg	90	90
β, deg	98.24(2)	100.80(4)
γ, deg	90	90
V, Å^3	1968.8(7)	2030(1)
Z	4	4
d_{calc}, g/cm^{-3}	2.524	2.527
color, form	white, prismatic	white, prismatic
data cryst dimens, mm	0.20 × 0.20 × 0.20	0.25 × 020 × 020
radiation	0.710 69	0.710 69
μ(Mo Kα), cm^{-1}	150.5	146.89
transm coeff	1.368−0.728	1.427−0.724
range of h, k, l measd	0, 12/0, 11/−32, 32	0, 15/0, 19/−19, 18
no. of rflcns measd (including stds)	5078	6423
no. of unique rflcns	4656	5883
no. of rflcns with $I \geq 3\sigma(I)$	3354	3664
no. of variables	218	227
R(F)[a]	0.040	0.063
R_w(F)[b]	0.049	0.076

[a] $R(F) = (\Sigma F_o| - |F_c|)/\Sigma|F_o|$. [b] $R_w(F)=[\Sigma w(|F_o| - |F_c|)^2/|F_o|^2]^{1/2}$; $[1/w = \sigma^2(F_o)]$.

absorption correction was performed by using the DIFABS program.[16] The structures were solved by Patterson methods and subsequent Fourier syntheses and least-squares refinements using the X-Ray 76 system[17] running on a VAX-3500 computer. Hydrogen atoms were placed in calculated positions with the exception of H1 and H8 for compound **1**, which were localized in the ΔF map. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms with isotropically thermal parameters. Crystal data and structure determination parameters are given in Table 1. Atomic coordinates and equivalent isotropic thermal parameters are listed in Table 2.

Results and Discussion

Heterobridged dinuclear gold(I) ring complexes $[Au_2(\mu\text{-L})(\mu\text{-}R_2P(CH_2)_nPR_2]$ (where L is the dianion of the purine derivatives given in Chart 1 were prepared in good yield by ligand substitution reactions of μ-bis(phosphine)bis(bromogold(I)) complexes with K_2L (prepared in situ from the reaction of the purine derivative with KOH in ethanol).

$$[(AuBr)_2(\mu\text{-}R_2P(CH_2)_nPR_2)] + K_2L \rightarrow [Au_2(\mu\text{-L})(\mu\text{-}R_2P(CH_2)_nPR_2)] + 2KBr$$

$$n = 2,\ R = CH_3;\ n = 1, 3, 4,\ R = Ph$$

These reactions do not depend on the stoichiometry of the reactants, since by using a 1:2 $[(AuBr)_2(\mu\text{-}R_2P(CH_2)_nPR_2)]$/purine derivative stoichiometry 1:1 complexes also were obtained. However, attempts to prepare 1:1 analogs with 1,2-bis(diphenylphosphine)hexane (dpph) were unsuccessful and resulted in the formation, in low yield, of complexes with all the ionizable protons substituted by $[Au(\mu\text{-dpph})AuBr]^+$ groups. In addition, when the purine derivative does not contain two ionizable protons in close positions, such as 3-methyl-8-ethylxanthine (H_2ME), coordination of the ligand to the gold atoms of the same $[Au_2(\mu\text{-}R_2P(CH_2)_nPR_2)]^{2+}$ moiety cannot be achieved and open ring complexes $[(HME)Au]_2(\mu\text{-}R_2P(CH_2)_n\text{-}PR_2)$ are obtained. Complexes are air and moisture-stable white solids.

Xanthine contains three acidic protons, two of which are attached to N1 and N3 in the pyrimidine ring, whereas the third proton is involved in a prototropic equilibrium N7−H ↔ N9−H. In the 2-fold negatively charged anion of xanthine, the remaining proton must be localized at N1, since this is the less acidic proton. In view of this, coordination of HX^{2-} and its analog MX^{2-} in dinuclear ring gold(I) complexes should take place through N3 and N9 neighboring positions. On the other hand, H_2TT has two ionizable protons in the imidazole ring that are involved in two types of tautomerism: prototropic N7−H ↔ N9−H and iminothiol−thioamide NH−C8═S ↔ N═C8−SH. When the imidazolic protons dissociate in basic medium, the sulfur atom must be the most probable binding site, since a soft polarizable metal such as gold(I) shows preference for the softer sulfur donor over the less polarizable nitrogen donor atoms. The second position of coordination may be N7 or N9, but the former must be favored over the latter because of the steric hindrance from the N3−CH_3 group. The results of the X-ray structure determinations for **1**, **2**, and **3** confirm the above proposed coordination modes for the ligands.

Dinuclear Ring Complexes. Crystal Structure Descriptions. $[Au_2(\mu\text{-HX})(\mu\text{-dmpe})]\cdot 3H_2O$ (1). The crystal structure of this complex consists of dinuclear gold(I) nine-membered ring molecules $[Au_2(\mu\text{-HX})(\mu\text{-dmpe})]$ and three lattice water molecules. Two perspective views of the structure are given in Figure 1 whereas selected bond lengths and angles are listed in Table 3. Inside the dinuclear molecule, the two gold atoms are bridged on one side by one bis(dimethylphosphine)ethane ligand, with Au1−P1 and Au2−P2 bond distances of 2.240(3) and 2.229(3) Å, respectively, and on the other side by a double-deprotonated xanthinate anion ligand coordinated through the N3 and N9 neighboring nitrogen atoms, with Au−N3 and Au−N9 distances of 2.071(9) and 2.047(1) Å. The Au-P and Au-N bond distances are within the range usually found for related complexes.[10] The coordination of gold atoms is almost linear with P1−Au1−N3 and P2−Au2−N9 angles of 175.5(3) and 177.9(3)°, respectively. The Au1−Au2 distance of 3.053(1) Å is between that observed for metallic gold (2.88 Å) and the sum

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Table 2. Positional Parameters for the Non-Hydrogen Atoms of the Complexes **1** and **2**

atom	*x*	*y*	*z*	U_{eq}, Å^2
		$[Au_2(\mu\text{-XH})(\mu\text{-dmpe})]$ (**1**)		
Au1	0.24471(5)	0.07072(5)	0.08948(2)	179(1)
Au2	0.33823(5)	−0.20186(5)	0.02410(2)	216(1)
P1	0.3398(3)	0.0071(4)	0.1754(1)	213(9)
P2	0.4713(3)	−0.3403(4)	0.0891(1)	236(9)
N1	0.0123(10)	0.3214(11)	−0.0449(4)	208(29)
C2	0.0760(12)	0.2749(13)	0.0066(5)	207(34)
O2	0.0662(10)	0.3629(10)	0.0460(4)	299(28)
N3	0.1464(9)	0.1417(11)	0.0127(4)	165(26)
C4	0.1553(12)	0.0587(14)	−0.0343(5)	196(33)
C5	0.0894(12)	0.0986(14)	−0.0873(4)	203(33)
C6	0.0105(12)	0.2418(14)	−0.0945(5)	220(35)
O6	−0.0498(11)	0.2963(11)	−0.1376(4)	362(31)
N7	0.1228(12)	−0.0096(13)	−0.1243(4)	303(35)
C8	0.2010(15)	−0.1120(14)	−0.0924(5)	273(38)
N9	0.2212(11)	−0.0765(12)	−0.0375(4)	233(30)
C11	0.4181(17)	−0.1848(18)	0.1840(6)	410(49)
C12	0.2053(15)	0.0038(24)	0.2203(6)	487(57)
C13	0.4736(18)	0.1401(21)	0.2054(7)	502(57)
C21	0.5356(16)	−0.2256(22)	0.1523(8)	506(58)
C22	0.6411(16)	−0.4029(21)	0.0688(8)	524(60)
C23	0.3970(20)	−0.5103(21)	0.1114(9)	613(69)
O11	0.7159(12)	−0.1483(14)	0.2989(5)	554(42)
O12	0.4529(13)	−0.1061(12)	0.3383(4)	477(38)
O13	0.8582(12)	0.0529(14)	0.2369(4)	497(39)
		$[Au_2(\mu\text{-TT})(\mu\text{-dmpe})]$ (**2**)		
Au1	0.30456(5)	0.22266(4)	0.03967(4)	309(2)
Au2	0.04444(5)	0.16157(4)	0.04022(5)	333(2)
S8	0.1226(4)	0.0724(3)	0.1800(3)	408(13)
P1	0.2750(4)	0.3939(3)	−0.0348(3)	389(13)
P2	−0.0512(4)	0.2457(3)	−0.0938(3)	393(13)
N1	0.6643(12)	0.0018(10)	−0.0935(4)	362(40)
C1	0.7873(16)	0.0192(17)	0.1289(10)	515(65)
C2	0.6521(14)	−0.0786(12)	0.1026(14)	349(45)
O2	0.7401(13)	−0.1362(11)	0.1820(11)	519(44)
N3	0.5401(12)	−0.0961(10)	0.2050(10)	378(41)
C3	0.5232(20)	−0.1749(15)	0.2112(10)	605(75)
C4	0.4447(13)	−0.0286(11)	0.2744(19)	307(42)
C5	0.4578(12)	0.0509(11)	0.1835(11)	297(40)
C6	0.5698(14)	0.0721(11)	0.1271(11)	333(44)
O6	0.5919(12)	0.1418(9)	0.0948(12)	505(46)
N7	0.3452(12)	0.0975(9)	0.0484(12)	310(36)
C8	0.2726(14)	0.0469(14)	0.1161(9)	372(48)
N9	0.3315(12)	−0.0344(9)	0.1669(11)	332(37)
C11	0.1352(19)	0.3762(15)	0.2100(10)	614(74)
C12	0.3949(21)	0.3974(18)	−0.1329(17)	612(77)
C13	0.2746(28)	0.4588(17)	−0.1043(18)	727(96)
C21	0.0052(25)	0.3641(15)	0.0526(21)	615(76)
C22	−0.2116(20)	0.2679(14)	−0.1033(17)	548(69)
C23	−0.0257(27)	0.1910(22)	−0.0908(12)	738(94)
O10	0.8703(20)	−0.1574(12)	−0.2114(14)	743(67)

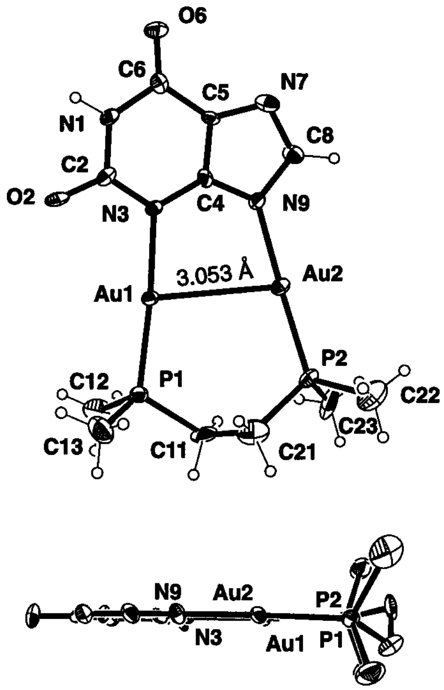

Figure 1. Front and side perspective views of $[Au_2(\mu\text{-HX})(\mu\text{-dmpe})]\cdot 3H_2O$, (**1**). The molecules of water are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex **1**, $[Au_2(\mu\text{-dmpe})(\mu\text{-HX})]\cdot 3H_2O$

Au1−Au2	3.053(1)	N1−C6	1.40(2)
Au1−P1	2.240(3)	C2−O2	1.25(2)
Au1−N3	2.071(9)	C2−N3	1.33(2)
Au2−P2	2.229(3)	C5−C6	1.44(2)
Au2−N9	2.05(1)	C5−N7	1.37(2)
N1−C2	1.38(2)	C6−O6	1.22(2)
N3−C4	1.37(2)	N7−C8	1.33(2)
C4−C5	1.40(2)	C8−N9	1.37(2)
C4−N9	1.33(2)		
Au2−Au1−N3	82.7(3)	N3−C4−C5	126.5(1.0)
P1−Au1−N3	175.5(3)	N3−C4−N9	125.6(1.1)
C2−N1−C6	127.3(1.0)	C5−C4−N9	107.9(1.0)
Au1−P1−C11	115.7(5)	C4−C5−C6	118.4(1.0)
Au1−Au2−P2	102.2(9)	C4−C5−N7	109.7(1.0)
Au1−Au2−N9	79.4(3)	C6−C5−N7	131.8(1.1)
P2−Au2−N9	177.9(3)	N1−C6−C5	112.0(1.0)
N1−C2−N3	120.1(1.0)	N1−C6−O6	120.8(1.1)
N1−C2−O2	117.7(1.1)	C5−C6−O6	127.2(1.1)
O2−C2−N3	122.2(1.1)	C5−N7−C8	102.8(1.0)
Au2−P2−C21	113.0(6)	N7−C8−N9	114.7(1.1)
Au1−N3−C2	120.7(8)	Au2−N9−C4	128.7(8)
Au1−N3−C4	122.6(7)	Au2−N9−C8	126.4(8)
C2−N3−C4	116.6(1.0)	C4−N9−C8	104.8(1.0)

of the van der Waals radii of 3.4 Å,[18] thus indicating metal−metal interaction. The slight deviations from linearity of the P−Au−N angles (2−5°) may be a consequence of the twisting of the ethylene chain in order to maximize the Au−Au interaction. This aurophilic interaction has been estimated to be 6−8 kcal/mol from the relative energies of different structural conformations of dinuclear gold(I) complexes.[2]

With the exception of the methylene and methyl groups of the bis(phosphine), the whole molecule can be considered as planar with maximum deviations from the least-squares plane through the nine ring atoms of 0.28 and 0.22 Å for O2 and N1, respectively.

Besides the Au−Au interaction, the structure of this complex exhibits important features. (a) The first is the expansion of the eight-membered ring usually found in dinuclear gold(I) ring complexes to a nine-membered ring. As far we know the only gold(I) complex of this type, whose structure has been determined by X-ray crystallography, is $[Au_2(\mu\text{-i-MNT})(\mu\text{-dppee})]$[13b] (where i-MNT is 1,1-dicyanoethene-2,2-dithiolate and dppee is bis(diphenylphosphino)ethylene). (b) The two bridging ligands are different and, moreover, one of them, the xanthinato ligand, coordinates gold(I) atoms through two nonequivalent positions. It should be pointed out that even though numerous examples of dinuclear gold(I) ring homobridged complexes exist, only a few examples of heterobridged derivatives have been reported so far, all of them containing symmetrical bridging ligands.[13] (c) This complex provides the only crystallographic evidence for a N3,N9 dianionic bridging coordination mode in a purine derivative. The N3,N9-coordination mode has been previously observed only in dimeric complexes of the type $[M(\mu\text{-hipoxanthine})_2(SO_4)_2(\mu\text{-}H_2O)_2(H_2O)_2]$ (where M is Cu(II),

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(18) Bondi, A. J. *J. Phys. Chem.* **1964**, *68*, 441.

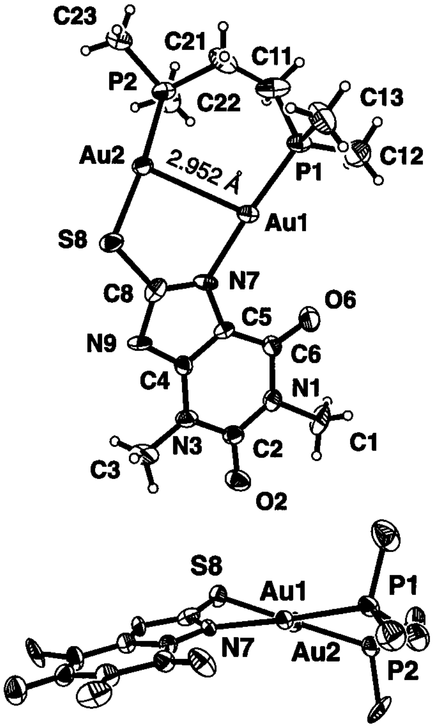

Figure 2. Front and side perspective views of $[Au_2(\mu\text{-TT})(\mu\text{-dmpe})]\cdot H_2O$ **(2)**. The molecule of water is omitted for clarity.

Co(II), Cd(II), and Zn(II))[19] and in the complex Cu(hypoxanthine)$_2Cl_2\cdot 3H_2O$,[20] but in all of them the purine ligand is found in neutral form.

Bond distances and angles in xanthine do not significantly differ from those reported for other compounds containing the same ring. As expected the xanthine is planar, with a maximum deviation from the least-squares plane of 0.03 Å for O2.

In the unit cell, centrosymmetrically related molecules are linked by a pair of complementary N1−H1···O2^i [$i = -x, 1 - y, -z$] hydrogen bonds, with a N···O distance of 2.828 Å. In addition, there is a extended hydrogen bond network involving the three water molecules and the O2, O6, and N7 atoms of the xanthine ligand.

$[Au_2(\mu\text{-TT})(\mu\text{-dmpe})]\cdot H_2O$ (2). A structure analogous to that of **1** was observed for **2**. The molecular structure is shown in Figure 2 whereas selected bond lengths and angles are given in Table 4. Again the gold atoms are bibridged by one dmpe ligand, with Au1−P1 and Au2−P2 distances of 2.221(5) and 2.249(4) Å, respectively, and by one 8-thiotheophyllinato dianion, with Au1−N7 and Au2−S8 bond distances of 2.05(1) and 2.297(4) Å, respectively, and exhibit linear coordination, P1−Au1−N7 = 175.0(4)° and P2−Au2−S8 = 174.3(2)°. As far as we are aware, the S/N chelate bridging coordination mode of thiotheophyllinato dianion in this compound has not been established for a thiopurine−metal complex so far.[21]

The Au−Au distance of 2.952 Å is shorter than that found for complex **1** despite the longer bite distance of the thiotheophyllinato ligand (2.737 Å) compared to that of HX^{2-} (2.414 Å). This fact can be explained by taking into consideration that the TT^{2-} is twisted in opposite direction to the methylene chain (see Figure 2), which causes the metal atoms to be in closer proximity. In the case of complex **1**, because the orbitals of N9 and N3 involved in the coordination to gold(I) atoms are restricted to be in the xanthine plane, any twist of the xanthine ligand from the plane containing the gold(I) and phosphorous atoms, to decrease the Au−Au distance, would lead to a decrease of the overlap between gold(I) and purine nitrogen orbitals, which ultimately would give an unfavorable result from the energy point of view. This seems to be the reason by which the xanthine ligand lies in the plane defined by the gold(I) and phosphorus atoms (see Figure 1), leading to a longer Au−Au distance.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complex **2**, $[Au_2(\mu\text{-dmpe})(\mu\text{-TT})]\cdot H_2O$

Au1−Au2	2.952(1)	C2−O2	1.25(2)
Au1−P1	2.221(5)	N3−C4	1.40(2)
Au1−N7	2.05(1)	C4−C5	1.37(2)
N1−C2	1.36(2)	C4−N9	1.35(2)
N1−C6	1.44(2)	C5−C6	1.40(2)
Au2−P2	2.249(4)	C5−N7	1.37(2)
Au2−S8	2.297(4)	C6−O6	1.21(2)
C8−N9	1.38(2)	N7−C8	1.34(2)
C2−N3	1.37(2)	S8−C8	1.71(2)
P1−Au1−N7	175.0(4)	C4−C5−C6	122.2(1.4)
Au2−Au1−P1	101.8(2)	C4−C5−N7	105.3(1.3)
Au2−Au1−N7	82.2(4)	C6−C5−N7	132.4(1.4)
C2−N1−C6	127.3(1.4)	N1−C6−C5	111.3(1.3)
Au1−P1−C11	116.4(8)	N1−C6−O6	121.5(1.5)
Au1−Au2−P2	98.2(2)	C5−C6−O6	127.1(1.5)
Au1−Au2−S8	87.4(1)	Au1−N7−C5	124.7(1.0)
S8−Au2−P2	174.3(2)	Au1−N7−C8	128.5(1.1)
N1−C2−N3	118.9(1.4)	C5−N7−C8	106.8(1.3)
N1−C2−O2	121.7(2)	N7−C8−N9	112.5(1.3)
O2−C2−N3	119.4(2)	S8−C8−N7	127.2(1.3)
C3−N3−C4	120.9(1.5)	S8−C8−N9	120.3(1.1)
N3−C4−C5	123.3(1.3)	Au2−S8−C8	103.9(5)
N3−C4−N9	123.5(1.4)	C4−N9−C8	102.2(1.3)
C5−C4−N9	113.1(1.3)	C5−C6−O6	127.1(1.5)

In the theophyllinato ligand, bond lengths and angles are similar to those observed for the related complex $[Au(HTT)(PPh_3)]$,[13b] in which the ligand binds to the gold(I) atom through S8. Compared to this latter compound, coordination at N7 in **2** only induces significant changes in the N7−C8−S8−N9 region. Thus the S8−C8−N7 angle of 127.2(13)° and the S8−C8−N9 angle of 120(3)° are about 6° larger and smaller, respectively, than those found in $[Au(HTT)(PPh_3)]$. This may be because of the twisting of the thiotheophyllinato ligand in **2**. The nine atoms of the purine systems are coplanar as expected, whereas small but significant deviations from planarity are observed for the exocyclic atoms as a consequence of the steric interactions between the methyl groups and the oxygen atoms.

In the crystal, dinuclear molecules are interconnected by water molecules through hydrogen bonds, which involve O2 and O6 atoms of the ligand with O2···O10 and O6···O10 acceptor−donor distances of 2.857(2) and 2.895(2) Å.

Crystals of $[Au_2(\mu\text{-MX})(\mu\text{-dmpe})]\cdot KBr\cdot 2H_2O$ (**3**) have also been examined by X-ray crystallography. Precession photographs showed 4/*mmm* Laue symmetry and systematic absences indicative of space groups *P*4*cc* or *P*4/*mcc*. Crystal data obtained on a CAD-4 diffractometer using Mo Kα radiation included the following: $a = 14.855(1)$ Å, $c = 19.667(1)$ Å, $Z = 8$, $D(\text{meas}) = 2.40(2)$ g cm^{-3}, intensity data (*hkl* 0/15, 0/15, 0/20), 3102 averaged to 867 observed reflections, and $R(\text{int}) = 0.078$. A Patterson solution for the positions of the two Au, K, and Br atoms was found in space group *P*4*cc*, but all the atoms of the ligands were not resolved in subsequent analyses due to disorder and twinning. However, the positions of the ligand donor atoms were obviously apparent, and refinement of the ligands as rigid groups converged to $R = 0.071$. We believe that the major features of the structure thus determined are correct, but the accuracy of the determination does not warrant

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(19) Dubler, E.; Hänggi, G.; Schmalle, H. *Inorg. Chem.* **1990**, *29*, 2518.

(20) Sletten, E. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1970**, *B26*, 1609.

(21) Dubler, E.; Gyr, E. *Inorg. Chem.* **1988**, *27*, 1466.

publication of atomic coordinates. The structure shows that the gold(I) atoms, at approximately 3.02 Å, are bridged by one dmpe and one N3, N9 chelating 1-methyl-8-ethyltheophyllinato dianion, with P1−Au1, P2−Au2, N3−Au1, and N9−Au2 distances of 2.23, 2.26, 2.14, and 2.03 Å, respectively.

Spectroscopic Properties of Gold(I) Ring Complexes. With regard to the bands concerning to the xanthine ligand, the IR spectra of 1 and its analogs with bis(diphenylphosphine)alkanes (n = 3,4) are very similar, thus suggesting the same coordination mode of xanthine in all these complexes. It should be noted that the spectrum of xanthine is considerably modified by complexation. The most obvious changes take place in the 2800−3000 cm^{-1} region, where only one N−H band is observed at about 2975 cm^{-1}, and in the 1700−1500 cm^{-1} region, where the bands due to the C=O groups appear at around 1690 and 1610 cm^{-1}. The former band, v(C6=O), is only slightly shifted to lower wavenumbers (about 10 cm^{-1}), whereas the latter, v(C2=O), is shifted to lower wavenumbers to a larger extent (about 60 cm^{-1}). These bands are primarily sensitive to the loss of the pyrimidine and imidazolic protons. In particular the relatively important shift of v(C2=O) supports the N3 atom being one of the coordination sites of the xanthinato dianion, since when N(3) binds to gold(I), electron distribution in the −N−C2=O region approximates to that of the corresponding anion $N(3)^{+}$=C2−O^{-}, leading to a reduction of the C2=O bond.[22]

The IR spectra of the complexes containing thiothephyllinato dianion show neither v(N−H) nor v(S−H) bands, as expected. In good accord with the loss of the imidazolic protons, the bands due to the C=O groups are shifted to lower wavenumber, about 25 cm^{-1} for v(C6=O) and about 15 cm^{-1} for v(C2=O).

In the ^{1}H-NMR spectra of **1** and **2** the phosphine methyl protons are seen as two well-separated doublets as result of the chemical nonequivalence of each dimethylphosphine part of the dmpe ligand and the coupling with the phosphorus atoms ($^2J_{P-H}$ = 11.3 Hz for **1** and $^2J_{P-H}$ = 10.9 and 11.2 Hz for **2**). The separation between the center of the doublets is more important for **2** (21 Hz) than for **1** (1.5 Hz), which agrees with a larger nonequivalence of the donor atoms (S8, N7) in the former compared with the latter (N3, N9). In **1** and its analog **3** (^{1}H-NMR spectra of **4** and **5** of enough quality could not be obtained due to the low solubility of the complexes) both N1−H and C8−H resonances undergo upfield shifts of about 1.0 and 0.8 ppm, respectively, with respect to their positions in the spectrum of the free xanthine, which may be because the large amount of electron density delocalized around the pyrimidine and imidazole ring has a shielding effect. Similar upfield shifts have been observed for those signals in other xanthine complexes, in which the imidazole and pyrimidine N−H protons have been substituted by methylmercury cations.[22] As for the complexes of thiotheophylline, their spectra show no N−H low field signals, as expected.

The ^{31}P NMR spectra (Table 5) of the complexes with 8-thiotheophylline consist of AX doublets, whereas those with xanthine and 1-methyl-8-ethyl-xanthine are typical of AB systems. These spectra are consistent with S8,N7 coordination in the former and N3,N9 coordination in the latter. The J_{P-P} coupling decreases as the number of connecting carbons (n) in the phosphine ligand backbone increases, as expected for the coupling process occurring through the phosphine ligand backbone.[23] According to this, the J_{P-P} coupling in dppp and dppb complexes is negligible. The general trend within these complexes is that when n increases, the phosphorus chemical shift becomes less positive. This trend is opposite to that observed for analogous dinuclear gold(I) ring complexes containing dithiolato ligands and for the free phosphines[24] and

Table 5. $^{31}P\{^1H\}$-NMR Data for Some of the Complexes[a]

complexes	δ, ppm ($^2J_{P-P}$, Hz)
$[Au_2(\mu\text{-HX})(\mu\text{-dmpe})]\cdot 3H_2O$ **(1)**	1.04, 1.03 (4.6)
$[Au_2(\mu\text{-TT})(\mu\text{-dmpe})]\cdot H_2O$ **(2)**	7.84, −2.08 (8.4)
$[Au_2(\mu\text{-MX})(\mu\text{-dmpe})]\cdot 2H_2O$ **(3)**	3.73, 2.11 (b)
$[Au_2(\mu\text{-HX})(\mu\text{-dppp})]$ **(4)**	34.31, 3.36 (b)
$[Au_2(\mu\text{-HX})(\mu\text{-dppb})]\cdot H_2O$ **(5)**	28.93, 29.25 (b)
$[Au_2(\mu\text{-TT})(\mu\text{-dppm})]$ **(6)**	37.68, 32.09 (56)
$[Au_2(\mu\text{-TT})(\mu\text{-dppp})]\cdot H_2O$ **(7)**	34.82, 28.83 (b)
$[Au_2(\mu\text{-TT})(\mu\text{-dppb})]$ **(8)**	32.71, 26.69 (b)
$[Au_2(HME)_2(\mu\text{-dppb})]\cdot H_2O$ **(11)**	33.33

[a] DMSO-d_6 solutions; reference 80% H_3PO_4. [b] Unresolved doublets.

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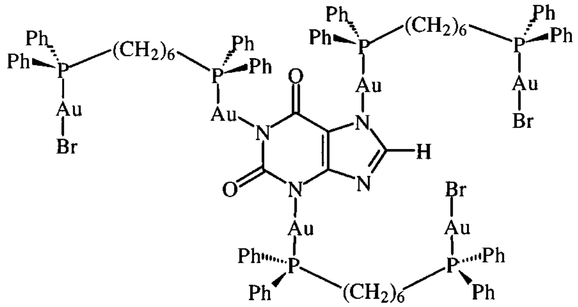

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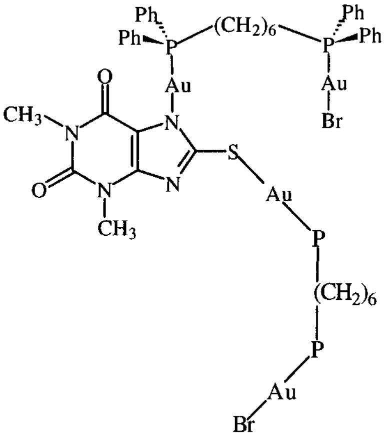

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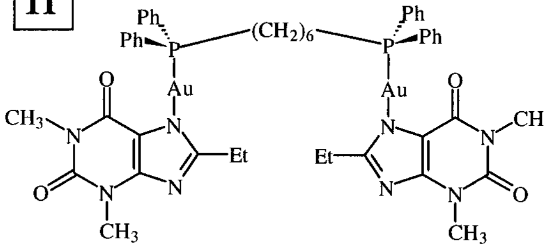

Figure 3. Proposed structures for $[Au_6(\mu_3\text{-X})(\mu\text{-dpph})_3Br_3]$ **(9)**, $[Au_4(\mu\text{-TT})(\mu\text{-dpph})_2Br_2]$ **(10)**, and $[Au_2(HME)_2(\mu\text{-dppb})]\cdot H_2O$ **(11)**.

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(24) Narayanaswamy, R.; Young, M. A.; Parkhurst, E.; Oullette, M.; Kerr, M. E.; Ho, D. M.; Elder, R. C.; Bruce, A. E.; Bruce, M. R. M. *Inorg. Chem.* **1993**, *32*, 2506.

most likely reflects small variations in dihedral or bond angles at phosphorus as *n* changes.

It should be noted at this point that, for the N3,N9 and S8,N7 bridging coordination modes that exhibit the purine derivatives in this complexes, the formation of ring and open ring oligomers with four or more gold atoms can not be ruled out. In principle, the formation of such type complexes should be favored as *n* increases in the series. However, the positive-ion fast atom bombardment (FAB) mass spectra for the dppb complexes, those with the higher *n* value, supports the cyclic dinuclear structure. The spectra are complex and difficult to be interpreted because of the existence of a significant amount of fragmentation and ion-molecule recombination. Nevertheless, for **5** and **8** the most intense peaks occur below *m*/*z* 1100 and the molecular peak (M) for **8** is observed at *m*/*z* 1031, which is consistent with a dinuclear ring structure. In view of this, we believe that all the complexes with $n = 1-4$ exhibit dinuclear cyclic structures, such as those observed for **1** and **2**. In these structures, despite the relatively small bite distance of the TT^{2-} and HX^{2-} dianions, the twisting of the methylene chain of the diphosphine ligand would allow the Au···Au interaction.

Open Ring Complexes. {(μ_3-X)[Au(μ-dpph)AuBr]$_3$} (9) and {(μ_2-TT)[Au(μ-dpph)AuBr]$_2$} (10). Information about the structure of the complexes {(μ_3-X)[Au(μ-dpph)AuBr]$_3$} and {(μ_2-TT)[Au(μ-dpph)AuBr]$_2$} has been primarily derived from IR spectroscopy and analytical data, since ^{1}H- and ^{31}P-NMR spectra of good enough quality could not be obtained because of the low solubility of the complexes in DMSO.

The IR spectra of the complexes **9** and **10** show no υ(NH) bands around 3000 cm^{-1}. This together with the increase in intensity that undergo the bands due to the bis(phosphine) ligand with respect to those of the purine ligand on going from the dinuclear ring complexes to **9** and **10** suggests that all the NH/SH ionizable protons of the ligands have been substituted by Au(μ-dpph)AuBr moieties. Thus, S8,N7 coordination of the TT^{2-} dianion is expected in **9** whereas N1,N3,N7 coordination of the X^{3-} ligand is expected in **10**. In the latter complex both υ(C2═O) and υ(C6═O) bands are significantly shifted to lower wavenumbers and appear as a wide band at 1618 cm^{-1}. This observation is consistent with the reduction of the C═O bond orders due to the binding of the Au(μ-dpph)AuBr groups at N1 and N3. In both complexes, coordination of the ligands through N7 must be favored over N9 to avoid the steric hindrance from the N3−CH_3 methyl group in the former and from the N3−Au(μ-dpph)AuBr moiety in the latter. According to this, the proposed structures of these complexes are as depicted in Figure 3. Indeed, the geometric requirements of the Au(μ-dpph)Au group prevents the formation of dinuclear ring complexes.

[(μ-dppb)Au(HME)$_2$] (11). 3-Methyl-8-ethylxanthine (H_2-ME) contains two ionizable protons, N1−H and that involved in the tautomeric equilibrium N7−H ↔ N9−H, the former being the less acidic proton. Therefore, the likely binding sites to gold(I) in this purine base must be N1 and either N7 or N9. It should be noted that, in contrast to the other purine derivatives ligands used in this study, the binding sites in H_2ME are not in close positions, thus preventing the formation of dinuclear ring complexes. According to this, the reaction of H_2ME with [(μ-dppb)(AuBr)$_2$] in a 1/1 mole ratio does not afford the dinuclear ring complex but the open ring complex [(μ-dppb)Au(HME)$_2$]. Since in the ir spectrum of this complex the υ(N1−H) band is present at 3147 cm^{-1} and the ^{1}H-NMR spectrum exhibits the N1−H signal at 10.55 ppm, coordination of the purine ligand must occur through one of the imidazolic protons, possibly N7 to avoid the steric hindrance from N3−CH_3. Therefore the structure proposed for this complex is as depicted in Figure 3. In good accord with this structure the ^{31}P NMR exhibits a singlet at 33.33 ppm.

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Supporting Information Available: Tables of crystallographic data H-atom coordinates, complete bond lengths and angles, anisotropic thermal parameters and intermolecular hydrogen bonding (32 pages). Ordering information is given in any current masthead page.

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