Co-ordination Chemistry of Dimethylgold(III). Synthesis, Spectroscopic, and Structural Studies* of Complexes with Neutral Aromatic Nitrogen-donor Ligands

Allan J. Canty and Nigel J. Minchin

Chemistry Department, University of Tasmania, Hobart, Tasmania, Australia 7001

Peter C. Healy

School of Science, Griffith University, Nathan, Queensland, Australia 4111

Allan H. White

Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, W.A. 6009

Dimethylgold(III) nitrate reacts with neutral ligands to form the complexes $[\text{AuMe}_2(\text{tpm})]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ (tpm = tri-2-pyridylmethane) and $[\text{AuMe}_2\text{L}]\text{NO}_3$ [L = tri-2-pyridylmethanol (tpmo), di-2-pyridylmethane (dpm), $\alpha\alpha$ -di-2-pyridyltoluene (dpt), di-1-pyrazolylmethane (dpzm), and tri-1-pyrazolylmethane (tpzm)]. The crystal structures of complexes of tpzm, tpm, and dpt have been determined by single-crystal X-ray diffraction at 295 K and refined by least-squares methods to $R = 0.033, 0.029$, and 0.042 for 3 043, 1 616, and 2 529 independent 'observed' reflections, respectively. In these structures the $[\text{AuMe}_2\text{L}]^+$ cations have essentially *cis*-square-planar co-ordination for gold(III), AuC_2N_2 , with $\text{Au}-\text{C}$ 2.023(7)—2.041(12) Å and $\text{Au}-\text{N}$ 2.127(8)—2.142(8) Å. In complexes of the potential tridentate ligands one pyridyl group is not co-ordinated in the tpm complex, and one pyrazolyl group is involved in a weak axial $\text{Au} \cdots \text{N}$ interaction [3.139(7) Å] in the tpzm complex. Comparison of the ^1H n.m.r. spectra of complexes of the potentially tridentate ligands (tpzm, tpm, and tpmo) with model complexes of bidentate ligands (dpzm, dpm, and dpt) suggests that the co-ordination behaviour of the ligands in methanol resembles that found in the solid state. Crystal data: $[\text{AuMe}_2(\text{tpzm})]\text{NO}_3$, monoclinic, space group $P2_1/n$, $a = 16.72(1)$, $b = 9.662(3)$, $c = 10.700(4)$ Å, $\beta = 107.83(3)^\circ$, $Z = 4$; $[\text{AuMe}_2(\text{tpm})]\text{NO}_3 \cdot 2\text{H}_2\text{O}$, orthorhombic, space group $P2_12_12_1$, $a = 18.56(1)$, $b = 11.150(7)$, $c = 9.983(7)$ Å, $Z = 4$; $[\text{AuMe}_2(\text{dpt})]\text{NO}_3$, monoclinic, $P2_1/n$, $a = 14.142(6)$, $b = 13.012(7)$, $c = 10.372(3)$ Å, $\beta = 100.60(3)^\circ$, $Z = 4$.

Reaction of the organometallic cations $[\text{Hg}^{\text{II}}\text{Me}]^+$ and $[\text{Au}^{\text{III}}\text{Me}_2]^+$ with unidentate ligands commonly leads to the formation of complexes with linear¹ and square-planar^{2,3} co-ordination geometries respectively. However, in the presence of some polydentate nitrogen-donor ligands (L), four-co-ordinate stereochemistry has been observed for Hg^{II} in complexes of the type $[\text{MeHgL}]\text{NO}_3$,⁴ and five-co-ordinate intermediates $[\text{AuMe}_2\text{L}]^+$ have been proposed in exchange processes.^{5,6} In particular, the tridentate tripod ligand tri-2-

pyridylmethanol (tpmo) binds as a tridentate ligand to HgMe^+ and thus this ligand, and similar ones such as tri-1-pyrazolylmethane (tpzm), may encourage five-co-ordination for gold with AuMe_2 [structure (A)]; alternatively, these ligands are not rigid and thus may allow the gold atom to adopt the common square-planar geometry with the ligand adopting a bidentate configuration as in (B).

We report in this paper a study of the structural chemistry and spectroscopic properties of $[\text{Au}^{\text{III}}\text{Me}_2]^+$ with the potentially tridentate ligands tpm, tpmo, and tpzm, and the related bidentate ligands di-2-pyridylmethane (dpm), $\alpha\alpha$ -di-2-pyridyltoluene (dpt), and di-1-pyrazolylmethane (dpzm).

X = H (tpm)
X = OH (tpmo)

tpzm

(A)

(B)

* Supplementary data available (No. SUP 23336; 39 pp.): thermal parameters, hydrogen atom geometries, ligand plane data, observed and calculated structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Experimental

The complexes $[\text{AuMe}_2\text{L}]\text{NO}_3$ were prepared using a modified method of that reported for the closely related complex $[\text{AuEt}_2(\text{bipy})]\text{NO}_3$ (bipy = 2,2'-bipyridyl),⁷ and similar to that used by Tobias and co-workers for interconversion of AuMe_2 halides⁸ and synthesis of AuMe_2 amino-acidato-complexes.⁹

The ligands dpzm and tpzm were used as received (Columbia Organic Chemicals Company, Inc.); the ligands dpm,¹⁰ tpm,¹¹ and dpt⁴ were prepared as described, and dimethylgold(III) iodide was prepared from $[\text{AuCl}_3(\text{py})]$ (py = pyridine) as previously described.¹² Microanalyses were by the Australian Microanalytical Service, i.r. spectra ($400\text{--}4\,000\text{ cm}^{-1}$) of complexes in Nujol and hexachlorobutadiene mulls were recorded with a Perkin-Elmer 577 spectrophotometer, ^1H n.m.r. spectra were recorded with a JEOL JNM-4H-100 spectrometer, and Raman spectra of crystalline solids were recorded with a Cary 82 laser Raman spectrometer over the range $100\text{--}4\,000\text{ cm}^{-1}$ using 514.5 nm excitation. Some of the complexes decomposed using this wavelength and these were

Table 1. Analytical and spectroscopic data

Complex	M.p. (decomp.) (°C)	Analysis (%) ^a			Λ_M^b $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$	$\nu(\text{AuC}_2)^c / \text{cm}^{-1}$	¹ H n.m.r. ^d
		C	H	N			
[AuMe ₂ (dpm)]NO ₃	193	35.0 (34.9)	3.6 (3.6)	9.1 (9.4)	89	583, 576	1.46, 6, s, Me; 4.69, 2, s, CH ₂ ; 7.90, 6, m, H(3,4,5); 8.73, 2, d, H(6)
[AuMe ₂ (dpt)]NO ₃	174	42.5 (42.6)	3.9 (3.8)	7.8 (7.8)	86	581, 569	0.95, 6, s, Me; 6.26, 1, s, CH; 6.68, 2, m, {Ph[H(2,6)]}; 7.32, 3, m, {Ph[H(3,4,5)]}; 7.80, 2, t, H(4); 8.25, 4, m, H(3,5); 8.76, 2, d, H(6)
[AuMe ₂ (tpm)]NO ₃ ·2H ₂ O	76–78	37.8 (37.9)	4.0 (4.1)	9.7 (9.8)	98	585, 574	1.02, 6, s, Me; 6.45, 1, s, CH; 7.70, 6, m, H(3,5); 8.14, 3, t, H(4); 8.68, 3, d, H(6)
[AuMe ₂ (tpmo)]NO ₃	115	39.2 (39.1)	3.7 (3.5)	10.1 (10.1)	96	584, 572	0.87, 6, s, Me; 7.6, 3, t, H(4), 8.10, 6, m, H(3,5); 8.62, 3, d, H(6)
[AuMe ₂ (dpzr)]NO ₃	127	24.7 (24.7)	3.2 (3.2)	16.1 (16.0)	91	582, 576	1.45, 6, s, Me; 6.90, 2, s, CH ₂ ; 6.67, 2, t, H(4); 8.05 and 8.28, 4, d, H(3,5)
[AuMe ₂ (tpzm)]NO ₃	84	28.6 (28.6)	3.3 (3.2)	19.4 (19.5)	85	583	1.34, 6, s, Me; 9.60, 1, s, CH; 6.60, 3, t, H(4); 8.06 and 8.27, 4, d, H(3,5)

^a Calculated values are given in parentheses. ^b In water. ^c Raman spectra of solid complexes, all $\nu(\text{AuC}_2)$ bands are very intense. ^d In CD₃OD; given as chemical shift, relative intensity, multiplicity, assignment.

satisfactorily re-examined with a Coherent Radiation dye laser Model 590 using Rhodamine 6G dye and with excitation in the range 580–590 nm. Conductivities were measured with a Philips PW 9504/00 conductivity meter in water.

[AuCl₃(py)].—As this compound is a convenient starting reagent for the synthesis of (AuMe₂I)₂,¹² the common method for recovery of gold from laboratory residues¹³ was modified to give this reagent directly. Gold residues were evaporated on a steam bath, concentrated hydrochloric acid was added, followed by evaporation to low volume on a steam bath, and slow heating to dryness on a hot plate. The solid material was fired to 800 °C in a furnace for 6 h, washed with warm water, and dissolved in *aqua regia*. The solution was reduced in volume to near dryness, concentrated hydrochloric acid added, and, while hot, the solution was filtered into a separating funnel. Auric acid (HAuCl₄) was extracted into ethyl acetate with continued addition of concentrated hydrochloric acid until the colour was discharged from the aqueous phase. The ethyl acetate solution was filtered and reduced in volume in a strong draught. Pyridine was added until crystallization of [AuCl₃(py)] ceased. The crystals were collected and washed with water.

Preparation of Complexes.—As all of the complexes were obtained in moderate yield (28–82%) by similar procedures the preparation of [AuMe₂(dpzm)]NO₃ is given as an example. Dimethylgold(III) iodide (0.524 g, 0.74 mmol) suspended in light petroleum (15 cm³, b.p. 40–60 °C) was added to a solution of silver nitrate (0.250 g, 1.47 mmol) in water (10 cm³), and the solution stirred for 2 h in a flask covered with foil to exclude light. The light petroleum was removed by rotary evaporation and the insoluble silver iodide removed by filtration to give an aqueous solution of dimethylgold(III) nitrate. Di-1-pyrazolylmethane (0.214 g, 1.45 mmol) was added with stirring until the ligand dissolved. On reduction of the volume in a strong draught, white crystals of the complex formed and were collected and recrystallized at room temperature from methanol–water (1 : 1) (yield 0.527 g, 82%).

Crystallography.—For each complex a unique data set was measured at 295 K within a preset $2\theta_{\text{max}}$ limit determined by the extent of the data; Syntex P1 and P2₁ four-circle diffractometers fitted with monochromatic Mo-K α radiation sources ($\lambda = 0.71069$ Å) were used in conventional 2θ – θ scan mode, yielding N independent reflections, N_0 of these with $I > 3\sigma(I)$ being considered 'observed' and used in the structure solution and refinement after the application of analytical absorption correction. Least-squares refinement was carried out using five blocks corresponding to the parameters of the AuMe₂, nitrate, and ring fragments. Hydrogen atom parameters were constrained to idealized estimates. Anisotropic thermal parameters were used for the non-hydrogen atoms. Residuals quoted for convergence are conventional R and R' , reflection weights being set at $w = [\sigma^2(F_o) + 0.0005(F_o)^2]^{-1}$. Neutral-atom scattering factors corrected for anomalous dispersion (f', f'')^{14–16} were employed. Computation used the X-RAY 76 program system¹⁷ implemented by S. R. Hall on a Perkin-Elmer 3240 computer. The results are given in Tables 2–6 and Figures 1–6.

Crystal data. [AuMe₂(tpzm)]NO₃ (1). C₁₂H₁₆AuN₃O₃, $M = 502.9$, Monoclinic, space group $P2_1/n$ (C_{2h}^5 , no. 14), $a = 16.72(1)$, $b = 9.662(3)$, $c = 10.700(4)$ Å, $\beta = 107.83(3)^\circ$, $U = 1.645(1)$ Å³, $D_m = 1.94(1)$, $Z = 4$, $D_c = 2.02$ g cm⁻³, $F(000) = 960$. Specimen: plate $0.30 \times 0.22 \times 0.07$ mm, $\mu(\text{Mo-K}\alpha) = 89$ cm⁻¹, $2\theta_{\text{max}} = 60^\circ$, $N = 4810$, $N_0 = 3043$, $R = 0.033$, $R' = 0.040$.

[AuMe₂(tpm)]NO₃·2H₂O (2). C₁₈H₂₃AuN₄O₅, $M = 571.6$, Orthorhombic, space group $P2_12_12_1$ (D_{2h}^4 , no. 19), $a = 18.56(1)$, $b = 11.150(7)$, $c = 9.983(7)$ Å, $U = 2.065(2)$ Å³, $D_m = 1.80(1)$, $Z = 4$, $D_c = 1.83$ g cm⁻³, $F(000) = 1112$. Specimen: plate $0.17 \times 0.16 \times 0.035$ mm, $\mu(\text{Mo-K}\alpha) = 71$ cm⁻¹, $2\theta_{\text{max}} = 50^\circ$, $N = 2096$, $N_0 = 1616$, $R = 0.029$, $R' = 0.032$.

[AuMe₂(dpt)]NO₃ (3). C₁₉H₂₀AuN₃O₃, $M = 534.9$, Monoclinic, space group $P2_1/n$ (C_{2h}^5 , no. 14), $a = 14.142(6)$, $b = 13.012(7)$, $c = 10.372(3)$ Å, $\beta = 100.60(3)^\circ$, $U = 1.877(1)$ Å³, $D_m = 1.89(1)$, $Z = 4$, $D_c = 1.89$ g cm⁻³, $F(000) = 1032$. Specimen: prism $0.10 \times 0.10 \times 0.15$ mm, $\mu(\text{Mo-K}\alpha) = 78$

Figure 1. Unit cell contents of $[\text{AuMe}_2(\text{tpzm})]\text{NO}_3$ (1); 20% thermal ellipsoids are shown for the non-hydrogen atoms and bonds in the coordination sphere about Au are shown as solid

cm^{-1} , $2\theta_{\text{max}} = 50^\circ$, $N = 3\,335$, $N_o = 2\,529$, $R = 0.042$, $R' = 0.050$.

Within each molecule, hydrogen atom labelling follows that of the parent carbon, those for the methyl group being suffixed A, B, C.

Results and Discussion

Preparation and Characterization of Complexes.—Evaporation to low volume of aqueous solutions containing equimolar quantities of ligand (L) and dimethylgold(III) nitrate, obtained by filtration of precipitated silver iodide from a mixture of dimethylgold(III) iodide and silver nitrate, gave crystals of the required complexes [equations (1) and (2)].

Infrared and Raman spectra indicate the presence of AuMe_2 , ligand, and nitrate groups with band positions altered from those of the unco-ordinated species. The Raman spectra have intense bands in the region expected for $\nu(\text{AuC}_2)$,^{8,18} and the complexes have molar conductivities in water that are characteristic of 1 : 1 electrolytes (Table 1).

Structures of the Complexes in Methanol.—Proton n.m.r. spectra of cations $[\text{HgMeL}]^+$ involving polydentate ligands containing pyridyl rings often reveal the mode of co-ordination of the ligands because unco-ordinated rings can adopt conformations resulting in increased shielding of the methyl group from ring-current anisotropy, e.g. for $\text{L} = 2$ -benzylpyridine a crystal structure determination¹⁹ has shown the methyl group to be above the plane of the phenyl ring, and the HgMe^1H resonance²⁰ occurs 0.29–0.36 p.p.m. upfield from unidentate pyridine²⁰ and bidentate di-2-pyridylmethane

Figure 2. Unit cell contents of $[\text{AuMe}_2(\text{tpm})]\text{NO}_3$ (2); see caption to Figure 1

complexes.¹¹ For the 2-benzylpyridine complex the orientation of the ring results from the presence of a weak Hg π interaction.¹⁹

Similarly, for $[\text{AuMe}_2\text{L}]^+$, the presence of an unco-ordinated ring, *e.g.* a pyrazolyl ring for $\text{L} = \text{tpzm}$, is expected to result in a chemical shift for the AuMe_2 protons upfield from that for the dpzm complex if conformation I is adopted, but similar to the dpzm complex if conformations II or III are adopted.

In the tpzm complex the AuMe_2 ^1H resonance has a chemical shift similar to those of the complexes of the bidentate ligands dpm and dpzm (1.34–1.46 p.p.m.) (Table 1), indicating conformation II or III for this complex. However, complexes involving dpt, tpm, and tpmo have the proton resonance 0.43–0.59 p.p.m. upfield from its position for the dpzm complexes, indicating conformation I, and consistent with tpm and tpmo being present as bidentate ligands with conformation I while tpzm is present as either tridentate (II) or bidentate (III).

Structures in the Solid State.—Aspects of the molecular geometry of complexes formed by tpzm, tpm, and dpt are given in Tables 2–6, and views of the cations $[\text{AuMe}_2\text{L}]^+$ are given in Figures 4–6.

The nitrate ions are regular (within 3σ in bond lengths and angles), planar, and are not co-ordinated to gold as oxygen

Table 2. Fractional atomic co-ordinates of complexes (1)–(3) with estimated standard deviations in parentheses

Atom	[AuMe ₂ (tpzm)]NO ₃ (1)			[AuMe ₂ (tpm)]NO ₃ ·2H ₂ O (2)			[AuMe ₂ (dpt)]NO ₃ (3)		
	x	y	z	x	y	z	x	y	z
<i>(i) Cation</i>									
Au	0.479 36(1)	0.108 38(2)	0.210 70(2)	0.348 71(2)	0.380 77(4)	0.399 74(5)	0.288 52(3)	0.266 26(3)	0.106 44(3)
methyl group 1									
C	0.388 2(5)	0.076 2(9)	0.038 7(8)	0.317 7(7)	0.380 5(14)	0.594 5(13)	0.169 0(8)	0.325 3(9)	0.163 1(12)
H(A)	0.390(—)	−0.010(—)	−0.010(—)	0.360(—)	0.413(—)	0.657(—)	0.120(—)	0.273(—)	0.197(—)
H(B)	0.335(—)	0.078(—)	0.054(—)	0.279(—)	0.438(—)	0.608(—)	0.200(—)	0.378(—)	0.224(—)
H(C)	0.390(—)	0.152(—)	−0.020(—)	0.305(—)	0.306(—)	0.625(—)	0.140(—)	0.390(—)	0.130(—)
methyl group 2									
C	0.499 2(6)	−0.099 2(8)	0.216 8(9)	0.242 1(6)	0.390 3(13)	0.350 7(15)	0.217 1(9)	0.129 3(9)	0.082 9(11)
H(A)	0.480(—)	−0.140(—)	0.290(—)	0.220(—)	0.440(—)	0.437(—)	0.260(—)	0.084(—)	0.138(—)
H(B)	0.465(—)	−0.141(—)	0.133(—)	0.234(—)	0.432(—)	0.269(—)	0.250(—)	0.093(—)	0.025(—)
H(C)	0.556(—)	−0.120(—)	0.226(—)	0.220(—)	0.312(—)	0.345(—)	0.171(—)	0.139(—)	0.133(—)
<i>(ii) Ligand</i>									
C	0.594 2(4)	0.388 7(6)	0.353 8(6)	0.474 3(5)	0.530 3(9)	0.280 5(12)	0.502 6(6)	0.308 7(8)	0.237 7(8)
H	0.618(—)	0.469(—)	0.406(—)	0.513(—)	0.583(—)	0.244(—)	0.568(—)	0.319(—)	0.281(—)
base: ring 1									
C,N(1)	0.605 1(3)	0.267 0(5)	0.438 5(5)	0.442 6(7)	0.456 4(10)	0.167 0(13)	0.502 3(7)	0.234 9(7)	0.125 5(9)
N(2)	0.571 8(3)	0.142 6(5)	0.397 0(6)	0.384 9(4)	0.386 3(9)	0.196 7(10)	0.417 2(6)	0.206 6(6)	0.053 2(7)
C(3)	0.602 3(4)	0.054 3(7)	0.497 6(7)	0.356 2(7)	0.315 2(10)	0.101 6(14)	0.414 7(8)	0.147 5(8)	−0.055 1(9)
H(3)	0.589(—)	−0.042(—)	0.499(—)	0.318(—)	0.262(—)	0.127(—)	0.352(—)	0.130(—)	−0.111(—)
C(4)	0.656 7(4)	0.126 6(7)	0.602 0(7)	0.382 3(8)	0.313 3(12)	−0.031 7(15)	0.497 4(11)	0.111 9(8)	−0.091 1(11)
H(4)	0.688(—)	0.091(—)	0.687(—)	0.364(—)	0.262(—)	−0.099(—)	0.494(—)	0.068(—)	−0.168(—)
C(5)	0.658 0(4)	0.259 3(7)	0.561 2(6)	0.438 0(8)	0.390 2(14)	−0.060 7(13)	0.584 8(9)	0.135 7(9)	−0.015 9(11)
H(5)	0.691(—)	0.377(—)	0.611(—)	0.458(—)	0.396(—)	−0.152(—)	0.644(—)	0.107(—)	−0.037(—)
C(6)				0.468 9(7)	0.460 1(12)	0.038 9(14)	0.588 1(8)	0.198 6(8)	0.092 0(10)
H(6)				0.510(—)	0.513(—)	0.020(—)	0.650(—)	0.217(—)	0.145(—)
ring 2									
C,N(1)	0.506 2(3)	0.416 3(5)	0.288 4(5)	0.506 2(5)	0.447 3(9)	0.385 9(12)	0.458 7(6)	0.409 8(7)	0.187 2(8)
N(2)	0.453 4(3)	0.324 3(8)	0.208 9(5)	0.460 2(4)	0.374 2(9)	0.448 6(8)	0.365 0(5)	0.409 0(6)	0.130 2(7)
C(3)	0.382 2(4)	0.394 3(8)	0.157 2(7)	0.485 7(7)	0.295 6(11)	0.537 4(13)	0.321 9(7)	0.497 6(8)	0.083 9(8)
H(3)	0.333(—)	0.353(—)	0.097(—)	0.452(—)	0.240(—)	0.584(—)	0.252(—)	0.497(—)	0.045(—)
C(4)	0.389 2(4)	0.526 7(8)	0.200 9(7)	0.557 5(7)	0.290 8(13)	0.570 3(13)	0.371 4(8)	0.589 5(8)	0.094 4(9)
H(4)	0.348(—)	0.602(—)	0.181(—)	0.573(—)	0.233(—)	0.640(—)	0.337(—)	0.654(—)	0.064(—)
C(5)	0.468 0(4)	0.539 9(7)	0.283 9(7)	0.604 5(6)	0.369 1(14)	0.508 9(13)	0.467 0(9)	0.591 0(9)	0.149 8(9)
H(5)	0.493(—)	0.621(—)	0.328(—)	0.655(—)	0.367(—)	0.532(—)	0.503(—)	0.656(—)	0.155(—)
C(6)				0.578 3(6)	0.446 5(11)	0.413 6(17)	0.511 3(7)	0.498 6(8)	0.197 2(9)
H(6)				0.610(—)	0.501(—)	0.369(—)	0.581(—)	0.496(—)	0.237(—)
ring 3									
C,N(1)	0.642 8(3)	0.379 7(5)	0.263 9(5)	0.422 5(6)	0.620 8(13)	0.340 5(12)	0.455 5(7)	0.265 8(7)	0.348 5(9)
N,C(2)	0.632 8(4)	0.274 6(6)	0.177 0(6)	0.432 6(6)	0.648 9(9)	0.468 6(11)	0.414 8(8)	0.333 6(9)	0.429 0(9)
H(2)							0.415(—)	0.410(—)	0.412(—)
C(3)	0.686 5(5)	0.303 4(10)	0.111 0(8)	0.388 1(9)	0.730 2(14)	0.525 8(16)	0.376 4(8)	0.294 3(10)	0.532 9(10)
H(3)	0.692(—)	0.248(—)	0.037(—)	0.400(—)	0.750(—)	0.691(—)	0.348(—)	0.342(—)	0.589(—)
C(4)	0.730 3(6)	0.423 4(12)	0.157 3(10)	0.334 5(9)	0.785 0(13)	0.455 1(18)	0.375 1(7)	0.189 9(11)	0.5549(10)
H(4)	0.732(—)	0.425(—)	0.156(—)	0.304(—)	0.840(—)	0.499(—)	0.347(—)	0.163(—)	0.625(—)
C(5)	0.700 8(5)	0.473 4(9)	0.255 3(8)	0.324 8(7)	0.758 8(13)	0.323 3(19)	0.414 1(7)	0.123 9(9)	0.479 8(10)
H(5)	0.717(—)	0.557(—)	0.307(—)	0.290(—)	0.803(—)	0.268(—)	0.414(—)	0.051(—)	0.499(—)
C(6)				0.367 6(7)	0.671 5(11)	0.262 8(13)	0.454 6(7)	0.160 0(8)	0.373 7(9)
H(6)				0.361(—)	0.645(—)	0.171(—)	0.480(—)	0.112(—)	0.321(—)
<i>(iii) Anion</i>									
N	0.326 4(4)	0.302 1(6)	0.424 5(5)	0.310 8(7)	0.085 8(9)	0.380 1(14)	0.732 1(7)	0.060 3(10)	0.286 9(9)
O(1)	0.285 3(4)	0.407 3(6)	0.432 4(6)	0.374 4(5)	0.109 1(10)	0.395 1(15)	0.784 4(7)	0.136 3(7)	0.309 5(8)
O(2)	0.295 2(3)	0.206 6(5)	0.350 6(5)	0.272 0(6)	0.063 6(11)	0.474 7(12)	0.657 6(6)	0.054 3(9)	0.330 5(9)
O(3)	0.400 7(4)	0.295 8(6)	0.491 8(6)	0.283 2(7)	0.086 2(11)	0.265 2(12)	0.755 4(7)	−0.009 5(9)	0.221 3(12)
<i>(iv) Solvent</i>									
O(1)				−0.009 5(5)	0.419 9(9)	0.2199 (10)			
O(2)				0.342 4(7)	0.063 6(12)	0.737 3(13)

Figure 3. Unit cell contents of $[\text{AuMe}_2(\text{dpt})]\text{NO}_3$ (3); see caption to Figure 1

Figure 4. Projection of $[\text{AuMe}_2(\text{tpzm})]^+$

atoms are at least 3.75 Å from gold, except for one contact of 3.067(10) Å in the *tpm* complex.

The pyrazolyl, pyridyl, and phenyl rings are planar in all the complexes, with all ring atoms within 0.02 Å of their mean planes. In all three complexes the gold atom has essentially square-planar geometry with the ligands present as bidentate *cis*- AuC_2N_2 , with angles C—Au—C 86.9(5)—87.4(6)°, C—Au—N 92.7(3)—94.5(4)°, and N—Au—N 84.8(3)—86.8(2)°. The gold

Figure 5. Projection of $[\text{AuMe}_2(\text{tpm})]^+$

atom is 0.02–0.34 Å from the mean planes of the co-ordinated pyrazolyl and pyridyl rings, and is 0.33 Å from the mean plane of the axial pyrazolyl ring. The planes of the co-ordinated rings form dihedral angles of 22.2°, 24.4° (*tpzm*) and 43.0–46.2° (*dpt* and *tpm*) with the mean plane of the *cis*- AuC_2N_2 group. Earlier structural determinations of AuR_2 complexes are of low accuracy,^{21–23} but the most recent example, $[\text{AuMe}_2(\text{OH})]_4$, has eight crystallographically independent Au—C bond lengths with a mean of 2.05 ± 0.08

Figure 6. Projection of $[\text{AuMe}_2(\text{dpt})]^+$ Table 3. Gold atom environment in the cations $[\text{AuMe}_2\text{L}]^+$; atoms derived from the methyl groups are italicized

L	tpzm	tpm	dpt
(i) Distances (Å)			
Au-C(1)	2.023(7)	2.028(13)	2.039(12)
Au-C(2)	2.031(8)	2.041(12)	2.040(11)
Au-N(12)	2.141(5)	2.136(10)	2.142(8)
Au-N(22)	2.129(5)	2.127(8)	2.141(8)
(ii) Angles (°)			
C(1)-Au-C(2)	87.0(3)	87.4(6)	86.9(5)
C(1)-Au-N(12)	177.5(11)	177.6(6)	177.9(6)
C(1)-Au-N(22)	92.7(3)	93.2(4)	93.9(4)
C(2)-Au-N(12)	93.3(3)	94.3(5)	94.5(4)
C(2)-Au-N(22)	176.9(5)	178.8(7)	179.2(12)
N(12)-Au-N(22)	86.8(2)	85.0(3)	84.8(3)

Table 5. Anion geometries in the complexes

	(1)	(2)	(3)
(i) Distances (Å)			
N-O(1)	1.244(9)	1.22(2)	1.23(1)
N-O(2)	1.223(7)	1.21(2)	1.22(1)
N-O(3)	1.233(8)	1.26(2)	1.22(2)
(ii) Angles (°)			
O(1)-N-O(2)	121.7(6)	121(1)	121(1)
O(1)-N-O(3)	118.6(6)	120(1)	119(1)
O(2)-N-O(3)	119.7(6)	118(1)	120(1)

Table 6. Gold environment planes in the cations $[\text{AuMe}_2\text{L}]^+$ of the complexes * (1)–(3)

	(1)	(2)	(3)
10^4p	8 668	374	1 912
10^4q	1 478	9 989	-2 315
10^4r	-4 763	279	9 539
<i>s</i>	5.441	4.613	0.986
σ	0.023	0.012	0.016
Au	0.040	-0.019	-0.011
C(1)	-0.004	0.011	0.018
C(2)	-0.016	-0.001	-0.012
N(12)	-0.004	0.010	0.017
N(22)	-0.015	-0.001	-0.012
C	1.003	1.700	1.668
C,N(11)	0.336	0.824	0.839
C(3)	-0.463	-0.827	-0.825
C,N(21)	0.269	0.827	0.772
C(23)	-0.548	-0.835	-0.829
N(32)	2.759	3.045	

* Least-squares planes are calculated through Au and its four nearest neighbours, and given in the form $pX + qY + rZ = s$, where the right hand orthogonal Å frame (X, Y, Z) has X parallel to a , Z in the ac plane; σ = standard deviation (Å) of defining atoms Au, C(1), C(2), N(12), and N(22); atom deviations are in Å; methyl C atoms are italicized.

Table 4. Ligand non-hydrogen geometries with estimated standard deviations in parentheses

Compound Ring (<i>n</i>)	$[\text{AuMe}_2(\text{tpzm})]\text{NO}_3$ (1)			$[\text{AuMe}_2(\text{tpm})]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ (2)			$[\text{AuMe}_2(\text{dpt})]\text{NO}_3$ (3)		
	1	2	3	1	2	3	1	2	3
(i) Distances (Å)									
C-C,N(n1)	1.462(8)	1.447(7)	1.440(9)	1.52(2)	1.52(2)	1.52(2)	1.51(1)	1.51(1)	1.54(1)
C,N(n1)-N(n2)	1.342(7)	1.355(7)	1.352(8)	1.36(2)	1.34(1)	1.33(2)	1.35(1)	1.35(1)	1.41(1)
C,N(n1)-C(n5,6)	1.342(7)	1.348(8)	1.350(10)	1.37(2)	1.37(2)	1.40(2)	1.41(2)	1.37(1)	1.40(1)
N(n2)-C(n3)	1.346(8)	1.333(8)	1.330(13)	1.35(2)	1.33(2)	1.35(2)	1.35(1)	1.35(1)	1.39(2)
C(n3)-C(n4)	1.392(9)	1.355(11)	1.380(14)	1.42(2)	1.37(2)	1.36(2)	1.37(1)	1.38(2)	1.38(2)
C(n4)-C(n5)	1.357(10)	1.350(9)	1.376(15)	1.37(2)	1.38(2)	1.36(3)	1.37(2)	1.37(2)	1.34(2)
C(n5)-C(n6)				1.39(2)	1.37(2)	1.39(2)	1.38(2)	1.40(2)	1.41(2)
(ii) Angles (°)									
Au-N(n2)-C,N(n1)	123.7(4)	123.1(3)		118.1(8)	119.5(7)		118.1(6)	119.5(6)	
Au-N(n2)-C(n3)	129.5(4)	131.0(4)		121.9(8)	121.4(8)		121.7(7)	120.9(6)	
C,N(n1)-C,N(n2)-C(n3)	106.6(5)	104.7(5)	104.3(6)	119.8(10)	119.1(9)	118.5(12)	120.0(9)	119.6(8)	119.3(11)
C,N(n1)-C-C,N(n1)+1,1)	111.3(5)	112.8(5)	112.1(5)	109.7(9)	112.2(10)	114.2(9)	110.2(7)	111.7(8)	113.9(8)
C-C,N(n1)-N(n2)	123.7(5)	123.6(5)	121.9(5)	117(1)	117(1)	117(1)	118.7(9)	117.1(8)	119.7(9)
C-C,N(n1)-C(n5,6)	124.8(5)	125.5(5)	124.7(6)	123(1)	122(1)	121(1)	121.7(8)	121.8(8)	121.1(9)
N(n2)-C,N(n1)-C(n5,6)	110.9(5)	110.5(4)	113.4(7)	120(1)	122(1)	123(1)	119.6(9)	121.1(8)	119.1(9)
N(n2)-C(n3)-C(n4)	108.5(6)	111.4(5)	110.8(9)	122(1)	122(1)	122(1)	121.5(9)	121.4(9)	120.6(11)
C(n3)-C(n4)-C(n5)	106.7(5)	106.3(6)	107.1(9)	116(1)	119(1)	120(1)	119.6(10)	119.5(10)	121.0(11)
C(n4)-C(n5)-N,C(n1,6)	107.2(5)	107.2(6)	104.4(8)	121(1)	119(1)	120(1)	119.3(12)	118.6(10)	120.5(11)
C(n5)-C(n6)-C,N(n1)				120(1)	119(1)	117(1)	119.9(9)	119.7(9)	119.5(10)

Å (average deviation from the mean),²³ similar to that for the present complexes, 2.023(7)—2.041(12) Å. The Au—N distances, 2.127(8)—2.142(8) Å, are similar to those noted for five-co-ordinate Au^{III} in [AuX₃(dmphen)] (dmphen = 2,9-dimethyl-1,10-phenanthroline, X = Cl or Br) * which have Au—N 2.09(1) (Cl) and 2.08(2) Å (Br),²⁴ for the nitrogen atom co-ordinated as part of the square plane AuX₃N.

In addition to functioning as bidentate ligands to give square-planar geometry for gold the ligands adopt conformation II (tpzm complex, with the mean plane of the axial pyrazolyl ring forming a dihedral angle of 86.6° with the AuC₂N₂ mean plane) or I (tpm and dpt complexes), but not III. There is no definite evidence of Au π interactions in the tpm and dpt complexes since, apart from C(31) which is apparently constrained by the ligand geometry to be close to gold in conformation I [3.064(12) Å (tpm), 3.114(8) Å (dpt)], the carbon and nitrogen atoms of the rings are all >3.44 Å from the gold atom.

Although the axial Au $\cdots$ N distance in the tpzm complex is long, 3.139(7) Å, the presence of a weak interaction is indicated since the gold atom lies 0.040 Å above the mean plane of the *cis*-AuC₂N₂ unit toward the axial nitrogen, whereas in the tpm and dpt complexes the gold atoms lie slightly below this plane [0.019 and 0.011 Å, respectively] (Table 6). The carbon and nitrogen atoms all lie below this plane in the tpzm complex, and the gold atom lies 0.050 Å above the mean plane defined by the carbon and nitrogen atoms.

Discussion

The crystallographic studies indicate the dominance of square-planar geometry in the chemistry of Au^{III}Me₂, and show the presence of a weak axial Au $\cdots$ N interaction in one complex and the flexibility of aromatic tripod ligands to bond as either bidentates or tridentates.

Despite the flexibility of the ligands, conformation III, involving the third potential donor group in an orientation well removed sterically from the gold atom, is not adopted in the complexes. The structures deduced for methanol solutions of the complexes from ¹H n.m.r. spectra, *i.e.* the presence of dpt and tpm in conformation I and tpzm in conformation II or III, are consistent with the solid-state configurations determined here.

The different behaviour of AuMe₂ toward tpzm and tpm may result from several factors. These include (i) the ligand geometry of tpzm compared with tpm and the preference for a dominant square-planar geometry with, at most, weak axial interactions (rotation of the axial pyridyl ring to allow co-ordination would result in a much shorter Au $\cdots$ N distance than in the tpzm complex), (ii) low basicity of tpzm compared with tpm,[†] and (iii) expected differences in 'softness,' and σ - and π -bonding characteristics of pyrazolyl and pyridyl rings.²⁶

* However, reaction of (AuEt₂Br)₂ with 1,10-phenanthroline (phen),⁷ and both (AuMe₂Cl)₂⁶ and (AuEt₂Br)₂⁷ with bipy give ionic complexes [AuR₂L][AuR₂X₂] (R = Me or Et, X = Br or Cl, L = phen or bipy), rather than five-co-ordinate analogues of [AuX₃(dmphen)] (X = Cl, Br).

† The base tpm has log K_H [pK_a of Htpm⁺ in 50% dioxan-water] 3.61,¹¹ but tpzm has log K_H < ca. 1.25.²⁵

Acknowledgements

We thank the Australian Research Grants Committee for financial support, C. V. Lee and E. E. George for assistance with ligand synthesis, the University of Tasmania for an honours scholarship (to N. J. M.), and the Education Department of Tasmania for leave of absence (to N. J. M.).

References

- 1 See, for example, D. L. Rabenstein, *Acc. Chem. Res.*, 1978, **11**, 100.
- 2 See, for example, B. Armer and H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 1970, **9**, 101; R. J. Puddephatt, 'The Chemistry of Gold,' Elsevier, New York, 1978; H. Schmidbaur, 'Gmelin Handbuch der Anorganischen Chemie. Organogold Compounds,' Springer-Verlag, Berlin, 1980.
- 3 G. C. Stocco, L. Pellerito, and N. Bertazzi, *Inorg. Chim. Acta*, 1975, **12**, 67.
- 4 A. J. Canty, N. Chaichit, B. M. Gatehouse, and E. E. George, *Inorg. Chem.*, 1981, **20**, 4293.
- 5 H. Hagnauer, G. C. Stocco, and R. S. Tobias, *J. Organomet. Chem.*, 1972, **46**, 179.
- 6 H. Schmidbaur and K. C. Dash, *J. Am. Chem. Soc.*, 1973, **95**, 4855.
- 7 M. E. Foss and C. S. Gibson, *J. Chem. Soc.*, 1949, 3063.
- 8 W. M. Scovell, G. C. Stocco, and R. S. Tobias, *Inorg. Chem.*, 1970, **9**, 2682.
- 9 R. S. Tobias, C. E. Rice, W. Beck, B. Purucker, and K. Bartel, *Inorg. Chim. Acta*, 1979, **35**, 11.
- 10 E. Leete and L. Marion, *Can. J. Chem.*, 1952, **30**, 563; A. J. Canty and C. V. Lee, unpublished work.
- 11 A. J. Canty, N. Chaichit, B. M. Gatehouse, E. E. George, and G. Hayhurst, *Inorg. Chem.*, 1981, **20**, 2414.
- 12 F. H. Brain and C. S. Gibson, *J. Chem. Soc.*, 1931, 762.
- 13 B. P. Block, *Inorg. Synth.*, 1953, **4**, 14.
- 14 D. T. Cromer and J. B. Mann, *Acta Crystallogr.*, 1968, **24**, 321.
- 15 D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.
- 16 R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.
- 17 'The X-RAY System, Version of March 1976,' Technical Report TR-446, ed. J. M. Stewart, Computer Science Centre, University of Maryland.
- 18 M. G. Miles, G. E. Glass, and R. S. Tobias, *J. Am. Chem. Soc.*, 1966, **88**, 5738; G. C. Stocco and R. S. Tobias, *J. Am. Chem. Soc.*, 1971, **93**, 5057; P. L. Kuch and R. S. Tobias, *J. Organomet. Chem.*, 1976, **122**, 429.
- 19 A. J. Canty, N. Chaichit, and B. M. Gatehouse, *Acta Crystallogr., Sect. B*, 1980, **36**, 786.
- 20 A. J. Canty and A. Marker, *Inorg. Chem.*, 1976, **15**, 425.
- 21 A. Burawoy, C. S. Gibson, G. C. Hampson, and H. M. Powell, *J. Chem. Soc.*, 1937, 1690.
- 22 R. F. Phillips and H. M. Powell, *Proc. R. Soc. London, Ser. A*, 1939, **173**, 147.
- 23 G. E. Glass, J. H. Konnert, M. G. Miles, D. Britton, and R. S. Tobias, *J. Am. Chem. Soc.*, 1968, **90**, 1131.
- 24 W. T. Robinson and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 1975, 726.
- 25 A. J. Canty and C. V. Lee, unpublished work.
- 26 See, for example, A. J. Canty and C. V. Lee, *Inorg. Chim. Acta*, 1981, **54**, L205.

Received 9th February 1982; Paper 2/242