Synthesis, Structure, and Properties of Trichloro- and Tribromo-(2,9-dimethyl-1,10-phenanthroline)gold(III)

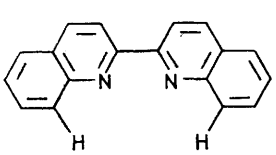
By **Ward T. Robinson,** Chemistry Department, University of Canterbury, Christchurch, New Zealand
Ekk Sinn,* Chemistry Department, University of Virginia, Charlottesville, Virginia 22901, U.S.A.

The title complexes [(4) Au(dmp)Cl_3 and (5) Au(dmp)Br_3, dmp = 2,9-dimethyl-1,10-phenanthroline] have been synthesised and their crystal and molecular structures determined from three-dimensional *X*-ray data obtained by counter methods. Crystals of (4) and (5) are not isomorphous though both are monoclinic, space group $P2_1/c$, with $Z = 4$ in unit cells of dimensions: (4) $a = 7{\cdot}343(1)$, $b = 18{\cdot}712(3)$, $c = 12{\cdot}143(3)$ Å, $\beta = 112{\cdot}29(2)°$; (5), $a = 8{\cdot}046(1)$, $b = 10{\cdot}478(3)$, $c = 20{\cdot}079(5)$ Å, $\beta = 92{\cdot}65(2)°$. The structures were solved by the heavy-atom method and refined by full-matrix least-squares to R 0·035 [(4) 904 reflections] and 0·060 [(5) 1122 reflections].

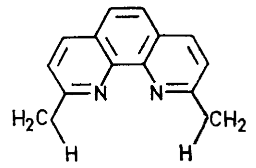
The compounds consist of discrete, diamagnetic five-co-ordinate molecules in both the solid state and in solution in aprotic solvents. The distribution of the ligands about the metal is approximately square pyramidal with the axial ligand displaced from the vertical, and at a relatively great distance from the metal, so that they may also be described as strongly distorted square planar. The direction of the distortion is such as to reduce the energy of the high-spin (triplet) state, but the magnitude is too low to produce a high-spin ground-state.

PLANAR geometry about the metal atom is strongly preferred in gold(III) complexes, although solution data have indicated that higher co-ordination numbers and some other kinds of association can occur.[1,2] In the solid, single-crystal *X*-ray structural determinations have been carried out on a five-[3] and a six-co-ordinated[4] complex. Although good crystals (and hence accurate data) could not be obtained with the latter (R 14%), the existence of six-co-ordinate gold(III) was established, with four short coplanar bonds and two very long bonds above and below the plane. The existence of an earlier six-co-ordinated complex[5] with even longer gold–ligand distances was controversial,[6-9] and this is perhaps better described as a square-planar complex with weak metal–halogen interactions above and below the plane.

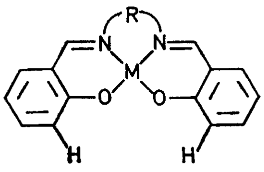
The five-co-ordinated complex, [Au(biq)Cl_3], contained five relatively strong bonds in a distorted trigonal bipyramidal configuration, the distortion being in the direction of a square pyramid. The ligand biq [2,2′-biquinolyl, (1)] together with several analogues, has been used in a general study of the use of steric hindrance in producing unusual stereochemistries, co-ordination numbers and magnetic properties.[3,10] The ligand 2,9-dimethyl-1,10-phenanthroline (2, dmp) is expected to produce similar though slightly greater † steric hindrance, and is expected to be more resistant to distortion because of the fused-ring backbone linking the dipyridyl skeleton. It should be possible to form five-co-ordinate gold(III) complexes with halides and (2) [or, for that matter (3)] {(4) [Au(dmp)Cl_3], (5) [Au(dmp)Br_3]}. The general form of the most likely structure for such complexes can be predicted *a priori* from steric and electrostatic considerations: gold(III) prefers planar geometry with the electronegative halogens as near as possible. Steric constraints prevent more than one halogen sharing the dmp plane, but the three halogens can be coplanar, with (2) perpendicular to this plane to minimise steric hindrance. Then co-ordination of either nitrogen of (2) necessarily brings the other nitrogen within bonding distance. Steric interaction will keep three chlorines and one nitrogen from being coplanar and the actual geometry will be a balance between the preference for a planar configuration, the bonding requirements of dmp, and steric strains. The slightly increased steric interaction might be expected to lead to a more regular trigonal bipyramid than is formed with (1).



(1)



(2)



(3)

The ligands (1) and (2) are approximate steric models for Schiff-base complexes of type (3) which may also act as ligands, and the gold(III) complexes of (1) and (2) will be structural models for the type of structure which

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† Slightly greater steric hindrance is expected from (2) than from (1) because the C–C aromatic bond linking the pyridine fragments in (2) is shorter than the corresponding single bond in (1), thus bridging the labelled H atoms closer together in (2) and allowing slightly less space for other ligands in the same plane. In addition, the aryl–methyl single bond in (2) is longer than the corresponding aromatic C–C bond in (1). Thus, the H atoms in (2) protrude further onto the other side of the metal, again leaving less room for other ligands in the same plane.

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is likely to occur in binuclear complexes involving gold(III) halides co-ordinated to (3).[10-12]

EXPERIMENTAL

Preparation of Compounds.—[Au(dmp)Cl_3], (3). Potassium tetrachloroaurate(III) (4 mmol) in methanol (40 ml) was added to dmp in benzene–methanol (40 : 20 v/v). The orange-yellow crystals which slowly formed were washed with benzene and methanol and dried *in vacuo* (Found: C, 32·9; H, 2·1; Au, 38·1; N, 5·2. $C_{14}H_{12}N_2AuCl_3$ requires C, 32·9; H, 2·3; Au, 38·5; N, 5·5%).

[Au(dmp)Br_3], (4). The foregoing procedure was repeated in the presence of an excess of tetramethylammonium bromide (30 mmol). The product formed as deep red crystals (Found: C, 30·3; H, 1·6; N, 4·3%. $C_{14}H_{12}N_2AuBr_3$ requires C, 30·5; H, 1·9; N, 4·4%).

Magnetic Susceptibility.—Measurements were made by the Gouy method, and the complexes were found to be diamagnetic.

Electrical Conductivity.—Measurements were made by use of a Phillips conductivity bridge (GM 4144) with cells of type PR 9412/01.

X-Ray Structure Analyses.—For both complexes, lattice constants and crystal-orientation parameters were obtained from least-squares refinements of the setting angles of 12 accurately centred reflections on a Hilger and Watts four-circle, computer-controlled diffractometer with Mo-K_α radiation. Crystal data are given in Table 1.

TABLE 1

Crystallographic data (distances in Å, angles in °), estimated standard deviations in parentheses

Compound	[Au(dmp)Cl_3]	[Au(dmp)Br_3]
No.	(4)	(5)
Space group	$P2_1/c$	$P2_1/c$
a	7·343(1)	8·046(1)
b	18·712(3)	10·478(3)
c	12·143(3)	20·079(5)
β	112·29(2)	92·65(2)
U/Å^3	1544	1691
D_m/g cm^{-3}	2·193	2·44
Z	4	4
D_c/g cm^{-3}	2·20	2·42
μ(Mo-K_α)/cm^{-1}	103·5	164·9
Crystal volume/mm^3	0·0010	0·0382
Max. transmission coefficient	0·563	0·123
Min. transmission coefficient	0·374	0·039

Zirconium-filtered Mo-K_α X-radiation and symmetric ω—2θ step scans were used to measure the intensities, with steps of 0·01° s^{-1} and scan ranges of 0·60° (4) and 0·72° (5). Stationary-crystal, stationary-counter background counts of $\frac{1}{4}$ the total scan time were measured at each end of the step-scan ranges. Attenuators were required to bring some reflections within the linear response range of the scintillation counter. The intensities of three standard reflections, monitored at regular intervals during data collection, were used to place all reflections in each data set on the same relative scales.

Initial corrections for background were made and intensities were then corrected for Lorentz and polarisation effects and for absorption using Gaussian integration. Calculations were carried out on an IBM 360/44 at the University of Canterbury with programs listed in ref. 13.

Finally, intensities from symmetrically equivalent reflections were averaged. For (4) 904 reflections and for (5) 1122 reflections were considered observed, having $I > 3\sigma(I)$, and were used in the subsequent refinements.

Solution and Refinement of the Structures.—In the full-matrix least-squares refinements, the function minimised was $\Sigma[w(|F_o| - |F_c|)^2]$ where the weight $w = 4F_o^2/\sigma^2(F_o^2)$. The weighted agreement factor R' is defined as: $\{\Sigma[w(|F_o| - |F_c|)^2]/\Sigma(wF_o^2)\}^{\frac{1}{2}}$.

Scattering-factor tables used for all atoms were calculated using the polynomial constants for HF SCF in ref. 14, the effects of anomalous dispersion of gold and halogen atoms being included [15] in F_c by use of the values for $\Delta f'$ and $\Delta f''$ in ref. 16.

In each structure, gold atom co-ordinates were obvious from Harker sections of Patterson syntheses and the remaining non-hydrogen atom positions were established by successive difference-Fourier syntheses with intermediate least-squares refinements. For (4) the data suggested that a more meaningful model would be obtained by refining anisotropic thermal parameters for the gold and halogen atoms separately while the outer carbon atoms could also be treated in this way for (5). In final structure-factor calculations, hydrogen atoms were included in positions calculated assuming C–H 1·0 Å, B 7·5 Å^2.

The relative weighting schemes appeared satisfactory since $\Sigma[w(|F_o| - |F_c|)^2]$ showed only slight dependence on $|F_o|$ and $\lambda^{-1}\sin\theta$. Structure-factor calculations for those low-intensity reflections not used in the refinements showed no anomalies of the type $|F_c| \gg |F_o|$. There was no evidence for secondary extinction and no anomalously high peaks appeared in final difference-Fourier syntheses. No variable parameters shifted by $>0·25\ \sigma$ during the last cycle of refinement. Observed and calculated structure amplitudes are listed in Supplementary Publication No. 21237 (3 pp., 1 microfiche).*

RESULTS AND DISCUSSION

Positional and vibrational parameters are listed in Tables 2 and 3 with their estimated standard deviations. Although the two crystal structures are not isomorphous, and are quite unrelated, the molecular structures are closely similar. Figure 1 is a view of (4) together with the ligand atom labelling scheme used in both structures, and Figure 2 shows a stereoscopic view of (5). Both structures consist of well-separated monomeric units and Figures 3 and 4 give the packing of the molecules in the unit cells. Intramolecular bond lengths and angles are given in Tables 4 and 5 respectively,

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

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TABLE 2

Final positional and thermal parameters for (4)

Atom	X	Y	Z	B/Å^2
Au	0·1442(1)	0·17147(3)	0·21081(6)	*
Cl(1)	−0·1103(7)	0·2147(3)	0·2633(4)	*
Cl(2)	0·0175(8)	0·2223(3)	0·0368(4)	*
Cl(3)	0·4120(7)	0·1333(3)	0·1837(4)	*
N(1)	0·271(2)	0·1325(7)	0·394(1)	3·5(3)
N(2)	0·006(2)	0·0442(7)	0·217(1)	3·9(3)
C(2)	0·394(3)	0·1772(9)	0·476(2)	4·5(4)
C(3)	0·477(3)	0·1495(9)	0·595(2)	4·6(4)
C(4)	0·438(3)	0·0838(10)	0·624(2)	4·9(4)
C(5)	0·271(3)	−0·0337(10)	0·560(2)	5·4(5)
C(6)	0·159(3)	−0·0754(10)	0·477(2)	5·3(5)
C(7)	−0·059(3)	−0·0933(9)	0·267(2)	5·3(5)
C(8)	−0·154(3)	−0·0685(10)	0·154(2)	5·8(5)
C(9)	−0·128(3)	0·0053(10)	0·128(2)	4·9(4)
C(10)	0·100(2)	0·0178(8)	0·327(1)	3·4(4)
C(11)	0·226(3)	0·0640(8)	0·417(1)	3·7(4)
C(12)	0·319(3)	0·0385(9)	0·536(2)	4·8(4)
C(13)	0·065(3)	−0·0533(9)	0·358(2)	4·6(4)
C(14)	0·415(3)	0·2479(10)	0·444(2)	5·1(5)
C(15)	−0·230(3)	0·0387(9)	0·011(2)	5·2(5)

* Anisotropic thermal parameters ($\times 10^3$; for Au $\times 10^4$) in the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{12}hl + 2\beta_{23}kl)]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Au	153(3)	212(3)	551(9)	−6(7)	17(1)	20(4)
Cl(1)	23(2)	46(2)	90(5)	21(5)	42(7)	−2(3)
Cl(2)	31(2)	42(2)	71(5)	8(5)	29(8)	21(3)
Cl(3)	25(2)	52(2)	85(5)	15(5)	65(7)	11(3)

and the principal intermolecular contacts are listed in Table 6. The most important least-squares planes are given in Table 7.

The gold atom is pulled out of the base of the square pyramid by 0·08 Å in (4) and 0·12 Å in (5). The main distortion from square pyramidal geometry is the elongated Au–N(2) bond, and the ' lean ' of the pyramid as defined by the angle [71·6° in (4), 70·2° in (5)] of the vertical plane [plane (II)] to the base. Another noteworthy feature is the distortion of the dmp ligand itself, especially in (4), where the angle between the extreme methylpyridine rings is 6·3°, representing significant curvature of the ligand.

Both complexes are essentially non-conductors in nitrobenzene [Λ_M 0·7 Ω^{-1} for a 3·1 × 10^{-3}M-solution of (4) and 0·6 Ω^{-1} for a 1 × 10^{-3}M-solution of (5)] suggesting retention of the molecular structure in solution, with both the dmp and the halide atoms co-ordinated. It was this fact which first suggested that a five-coordinate structure would be likely. The small conductivities observed suggest that a small degree of decomposition or dissociation occurs in solution. The complexes are diamagnetic, like all gold(III) complexes studied so far, indicating that the energy of $d_{x^2-y^2}$ is high compared to that of the other d orbitals.

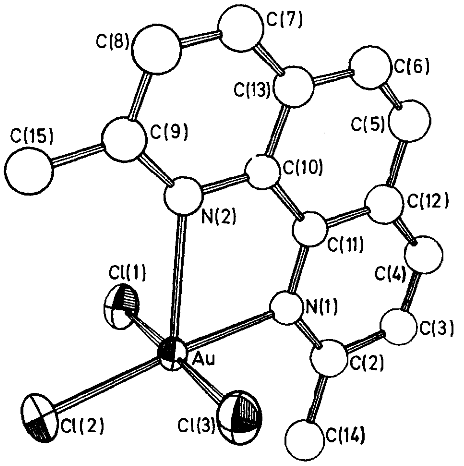

FIGURE 1 The molecule of [Au(dmp)Cl$_3$], (4), showing the ligand atom numbering system used for both compounds in the crystallographic analysis

Gold(III), d^8, is analogous to nickel(II), d^8. In square-planar nickel(II) the elevation of $d_{x^2-y^2}$ above the other

TABLE 3

Final positional and thermal parameters for (5)

Atom	X	Y	Z	B/Å^2	Atom	X	Y	Z	B/Å^2
Au	0·2552(1)	0·1959(1)	0·15624(5)	*	C(6)	0·266(9)	0·491(4)	−0·080(2)	*
Br(1)	0·5544(4)	0·2184(4)	0·1678(2)	*	C(7)	0·288(10)	0·249(6)	−0·105(3)	*
Br(2)	0·2700(5)	−0·0130(4)	0·2050(2)	*	C(8)	0·286(9)	0·130(4)	−0·086(2)	*
Br(3)	−0·0445(4)	0·1921(4)	0·1536(2)	*	C(9)	0·266(4)	0·108(4)	−0·018(2)	5·5(8)
N(1)	0·242(3)	0·385(2)	0·124(1)	3·9(5)	C(10)	0·263(3)	0·321(3)	0·009(1)	3·6(6)
N(2)	0·256(3)	0·196(3)	0·026(1)	5·1(5)	C(11)	0·247(3)	0·416(3)	0·056(1)	2·9(5)
C(2)	0·227(4)	0·473(4)	0·171(2)	4·9(7)	C(12)	0·243(5)	0·543(3)	0·039(2)	5·8(8)
C(3)	0·226(6)	0·603(4)	0·156(2)	*	C(13)	0·270(5)	0·360(4)	−0·059(2)	6·1(8)
C(4)	0·229(7)	0·642(4)	0·088(2)	*	C(14)	0·231(5)	0·440(3)	0·243(2)	*
C(5)	0·254(8)	0·583(5)	−0·029(2)	*	C(15)	0·264(7)	−0·033(3)	0·006(2)	*

* Anisotropic thermal parameters

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Au	0·0112(2)	0·0064(2)	0·00225(4)	−0·0001(2)	0·00001(6)	0·00064(6)
Br(1)	0·0123(5)	0·0142(5)	0·0047(1)	0·0011(4)	−0·002(2)	0·0014(2)
Br(2)	0·0268(7)	0·0087(4)	0·0046(2)	0·0006(5)	−0·0000(3)	0·0026(2)
Br(3)	0·0122(5)	0·0183(6)	0·0057(1)	−0·0026(5)	0·0001(2)	0·0038(3)
C(3)	0·04(1)	0·014(6)	0·005(2)	0·008(7)	0·002(4)	0·001(3)
C(4)	0·06(2)	0·012(5)	0·004(1)	0·003(7)	0·004(4)	−0·001(2)
C(5)	0·07(2)	0·019(7)	0·004(1)	0·01(1)	0·001(4)	0·001(3)
C(6)	0·10(3)	0·009(5)	0·004(1)	0·002(9)	0·005(5)	0·002(2)
C(7)	0·07(2)	0·03(1)	0·004(2)	−0·01(1)	−0·004(5)	−0·004(4)
C(8)	0·10(3)	0·007(5)	0·005(2)	−0·001(10)	−0·004(5)	0·002(2)
C(14)	0·036(9)	0·009(4)	0·003(1)	0·001(5)	0·002(3)	0·001(2)
C(15)	0·05(1)	0·005(4)	0·006(2)	−0·003(6)	−0·003(4)	−0·001(2)

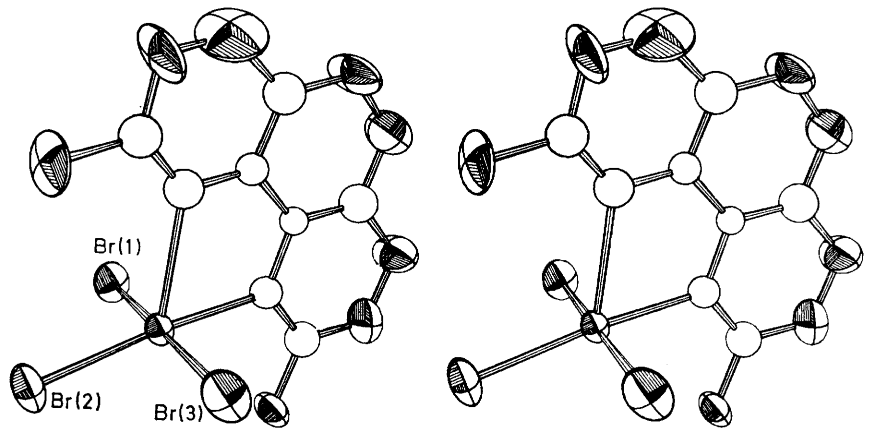

FIGURE 2 A stereoview of (5), [Au(dmp)Br_3]

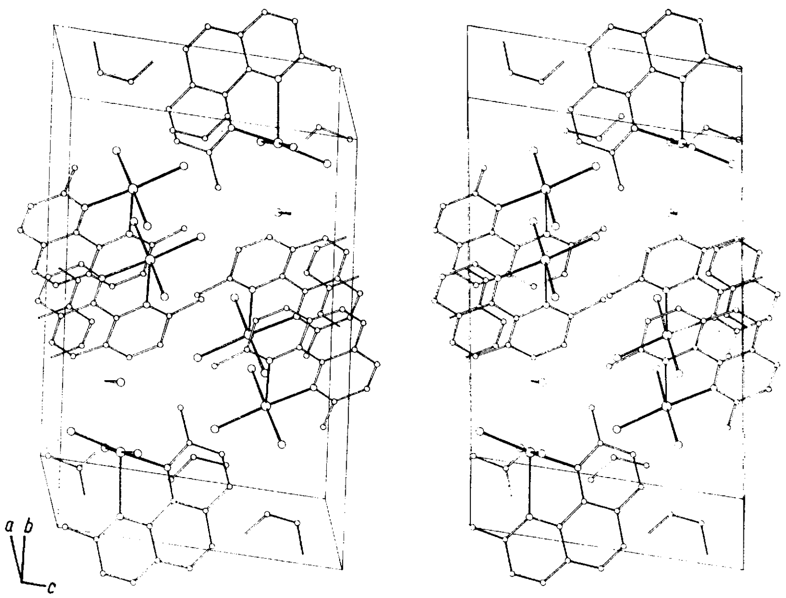

FIGURE 3 Packing of (4) in the unit cell

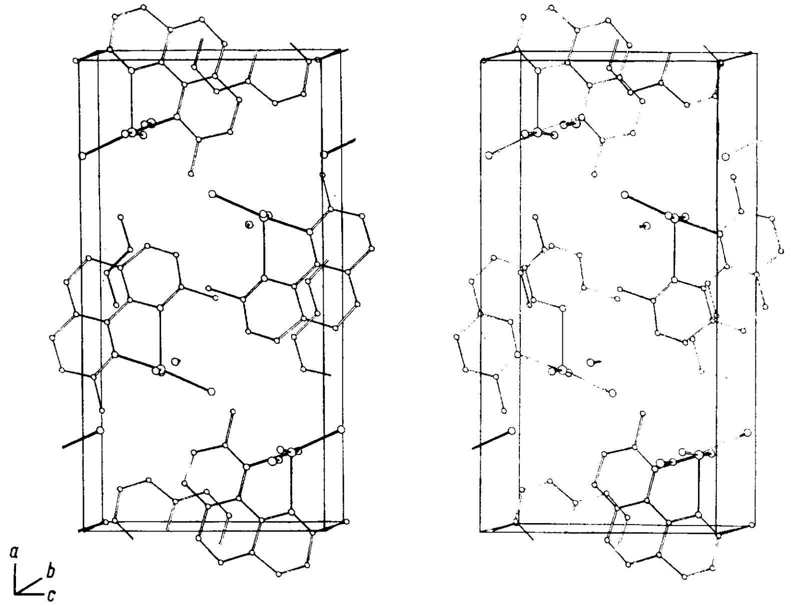

FIGURE 4 Packing of (5) in the unit cell

TABLE 4

Bond lengths (Å)

	(4)	(5)		(4)	(5)
Au–X(1) *	2·275(5)	2·419(3)	C(4)–C(12)	1·39(2)	1·44(5)
Au–X(2)	2·267(4)	2·398(4)	C(11)–C(12)	1·43(2)	1·38(4)
Au–X(3)	1·285(5)	2·410(3)	C(5)–C(12)	1·46(2)	1·43(5)
Au–N(1)	2·09(1)	2·08(2)	C(5)–C(6)	1·29(2)	1·41(6)
Au–N(2)	2·58(1)	2·61(2)	C(6)–C(13)	1·42(2)	1·44(5)
N(1)–C(2)	1·35(2)	1·33(4)	C(10)–C(13)	1·43(2)	1·43(4)
N(1)–C(11)	1·38(2)	1·41(3)	C(7)–C(13)	1·36(2)	1·50(6)
N(2)–C(9)	1·37(2)	1·29(4)	C(7)–C(8)	1·36(2)	1·30(6)
N(2)–C(10)	1·34(2)	1·35(4)	C(8)–C(9)	1·44(2)	1·40(5)
C(2)–C(14)	1·46(2)	1·48(4)	C(9)–C(15)	1·48(2)	1·56(5)
C(2)–C(3)	1·43(2)	1·39(6)	C(10)–C(11)	1·42(2)	1·38(4)
C(3)–C(4)	1·34(2)	1·42(5)			

* (4) X = Cl, (5) X = Br.

TABLE 5

Bond angles (°)

	(4)	(5)
N(1)–Au–X(1)	88·8(4)	88·6(6)
N(1)–Au–X(2)	175·5(4)	174·1(6)
N(1)–Au–X(3)	90·0(4)	88·3(6)
N(1)–Au–N(2)	73·2(5)	71·9(9)
X(1)–Au–N(2)	88·7(3)	92·7(5)
X(2)–Au–N(2)	111·2(3)	114·0(6)
X(3)–Au–N(2)	94·1(3)	91·5(6)
X(1)–Au–X(2)	90·6(2)	91·1(1)
X(2)–Au–X(3)	90·4(2)	91·4(1)
X(3)–Au–X(1)	176·5(2)	173·7(1)
C(9)–N(2)–C(10)	122·4(13)	120·9(27)
Au–N(2)–C(10)	106·0(10)	105·0(18)
Au–N(2)–C(9)	131·6(11)	133·8(23)
Au–N(1)–C(11)	118·8(10)	121·3(20)
Au–N(1)–C(2)	116·4(10)	116·1(20)
C(2)–N(1)–C(11)	124·8(14)	122·5(26)
N(1)–C(2)–C(14)	122·1(15)	122·0(30)
N(1)–C(2)–C(3)	115·3(15)	121·5(32)
C(3)–C(2)–C(14)	122·5(16)	116·1(34)
C(2)–C(3)–C(4)	123·3(17)	119·0(39)
C(3)–C(4)–C(12)	119·2(17)	117·6(36)
C(6)–C(5)–C(12)	122·4(18)	120·3(42)
C(5)–C(6)–C(13)	122·8(18)	115·9(36)
C(8)–C(7)–C(13)	123·9(17)	123·9(49)
C(7)–C(8)–C(9)	119·0(17)	116·5(45)
C(8)–C(9)–C(15)	123·6(16)	117·0(34)
C(8)–C(9)–N(2)	117·0(15)	124·8(33)
N(2)–C(9)–C(15)	119·2(15)	118·2(30)
N(2)–C(10)–C(11)	118·4(14)	121·3(24)
C(11)–C(10)–C(13)	120·0(15)	116·9(28)
N(2)–C(10)–C(13)	121·5(15)	121·5(27)
N(1)–C(11)–C(10)	123·3(14)	119·9(25)
N(1)–C(11)–C(12)	117·2(15)	117·8(26)
C(10)–C(11)–C(12)	119·5(15)	122·2(26)
C(4)–C(12)–C(11)	119·9(16)	121·5(31)
C(4)–C(12)–C(5)	122·8(17)	117·4(37)
C(5)–C(12)–C(11)	117·2(17)	121·1(36)
C(6)–C(13)–C(7)	126·0(17)	124·3(39)
C(7)–C(13)–C(10)	115·8(16)	112·2(35)
C(6)–C(13)–C(10)	118·1(16)	123·6(34)

TABLE 6

Principal intermolecular contacts (Å)

(*a*) In (4)

Cl(1) · · · Cl(2′)	3·307	Cl(2) · · · C(15′)	3·843
Cl(1) · · · N(2′)	3·405	Cl(3) · · · C(5′)	3·616
Cl(1) · · · Cl(3′)	3·604	Cl(3) · · · C(2′)	3·690
Cl(1) · · · C(2′)	3·691	Cl(3) · · · C(14′)	3·743
Cl(1) · · · C(11′)	3·746	Cl(3) · · · C(11′)	3·803
Cl(1) · · · C(7′)	3·863	C(3) · · · C(6′)	3·407
Cl(1) · · · C(14′)	3·877	C(5) · · · C(13′)	3·409
Cl(2) · · · C(2′)	3·647	C(5) · · · C(10′)	3·493
Cl(2) · · · C(14′)	3·757	C(12) · · · C(12′)	3·414

(*b*) In (5)

Br(1) · · · C(14′)	3·798	Br(3) · · · C(14′)	3·720
Br(1) · · · C(6′)	3·831	Br(3) · · · C(5′)	3·775
Br(1) · · · C(5′)	3·857	C(8) · · · C(14′)	3·516
Br(1) · · · C(11′)	3·866		

orbitals is sufficient to produce spin-pairing in all well-established cases so far examined. Ligand-field splittings increase from the first- to the third-transition series, and with increasing oxidation number of the metal atom, so that the ligand-field splitting in gold(III) should be at least twice as great as in the nickel(II) analogue. Consequently the splitting between $d_{x^2-y^2}$ and the other *d* orbitals should be much greater in planar gold(III) than in nickel(II), with no prospect of a high-spin ground-state. The positioning of one or two extra ligands along the *x* axis [perpendicular to the plane of a square-planar gold(III) complex] raises the energy of d_{z^2} with respect to the other *d* orbitals, and production of a high-spin complex depends on reducing the d_{z^2}–$d_{x^2-y^2}$ separation to the magnitude of the electron-pairing energy. Clearly the six-co-ordinate complex[4] [Au(pda)$_2$I$_2$]I [pda = *O*-phenylenebis(dimethylarsine)] fails to do this because the Au–I bonds along the *z* axis are very long (3·35 Å) compared to the sums of the covalent radii for these atoms (1·40 + 1·33 = 2·73 Å) though still shorter than the non-bonded distance (2·2 + 2·2 = 4·4 Å).[4,17] The interaction with d_{z^2} is thus minimal. In (4) and (5), the extra bond 'along' the *z* axis, Au–N(2), is weak [2·61 (4) and 2·58 Å (5); covalent Au–N = 1·40 + 0·74 = 2·04 Å; non-bonded Au–N 2·2 + 1·5 = 3·7 Å] and it is displaced from the *z* axis, again minimising the interaction of d_{z^2} with the ligand. If [Au(biq)Cl$_3$] is also to be square pyramidal, the bond corresponding to Au–N(2) has to be shorter (2·40 Å) but the ligand is displaced 0·74 Å from the *z* axis which again minimises interaction with d_{z^2}.

The results so far indicate that not only are complexes with higher co-ordination numbers >4 rare with gold, but in all known cases where a higher co-ordination number has been forced on the metal, the stereochemistry adopted was such as to minimise the possibility of a high-spin ground-state.

Compared to [Au(biq)Cl$_3$],[3] (4) has a markedly lengthened Au–N(2) bond (2·58 from 2·40 Å) and shortened Au–N(1) bond (2·09 from 2·28 Å). This is attributable to the greater steric repulsion of Cl(2) by the methyl group C(15) compared to a ring C–H group in biq. This change between the two complexes corresponds to a rotation (clockwise as seen in Figure 2) of the bidentate ligand, which is preferred over a displacement (counter-clockwise in Figure 2) of the Au–Cl(2) bond. Replacement of Cl(2) by Br(2) in [Au(dmp)Br$_3$] produces a slight further rotation of the dmp ligand, as manifested by a further lengthening of the Au–N(2) bond to 2·61 Å [and a shortening of the Au–N(1) bond which is probably significant].

The other differences between [Au(biq)Cl$_3$] and [Au(dmp)Cl$_3$] are dramatic: the Au–Cl(1) and Au–Cl(3) bonds are shortened in [Au(dmp)Cl$_3$] (2·28 and 2·29 from 2·35 and 2·38 Å) while the Au–Cl(2) bond is lengthened (2·27 over 2·09 Å). All three Au–Cl bonds in [Au(dmp)Cl$_3$] [and all three Au–Br bonds in (5)]

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[17] L. E. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960.

TABLE 7

Coefficients of least-squares planes, equations in the form $AX + BY + CZ = D$, for (4) [Au(dmp)Cl_3] and for (5) [Au(dmp)Br_3]. Distances (Å) of relevant atoms from the planes are given. Data for (4) are given before those for (5)

Plane	Atoms in plane	*A*	*B*	*C*	*D*	Distances
(I)	Cl(1)—(3), N(1)	0·3837	0·8588	0·3396	3·6880	Cl(1) 0·009, C(2) −0·009, Cl(3) 0·009, N(1) −0·010, Au 0·076
	Br(1)—(3), N(1)	0·0759	−0·3598	−0·9299	−3·6250	Br(1) −0·001, Br(2) 0·001, Br(3) −0·001, N(1) 0·002, Au 0·117
(II)	Au, Cl(1), Cl(3), N(2)	−0·1737	0·0966	−0·9801	2·1466	Au 0·028, Cl (1) −0·014, Cl(3) −0·014, N(2) 0·001
	Au, Br(1), Br(3), N(2)	−0·0556	0·9981	−0·0263	1·9248	Au −0·065, Br(1) 0·031, Br(3) 0·031, N(2) 0·002
(III)	Au, Cl(2), N(1), N(2)	0·9046	−0·3738	−0·2050	−1·6727	Au 0·009, Cl(2) −0·004, N(1) −0·005, N(2) 0
	Au, Br(2), N(1), N(2)	−0·9972	−0·0559	−0·0490	−2·1707	Au −0·001, Br(2) 0, N(1) 0, N(2) 0
(IV)	Ligand dmp	0·9138	−0·3358	−0·2285	−1·7086	Au 0·109, C(2) 0·180
	Ligand dmp	−0·9940	−0·0274	−0·1058	−2·1736	Au 0·111, Br(2) −0·228
(V)	N(1), C(2)—(4), C(11), C(12), C(14)	0·9133	−0·3641	−0·1827	−1·5266	
	N(1), C(2)—(4), C(11), C(12), C(14)	−0·9951	−0·0492	−0·0853	−2·2365	
(VI)	N(2), C(7)—(10), C(13), C(15)	0·9164	−0·2968	−0·2685	−1·8084	
	N(2), C(7)—(10), C(13), C(15)	−0·9902	−0·0103	−0·1390	−2·1135	

Interplanar angles (°)

	(I)–(II)	(I)–(III)	(I)–(IV)	(II)–(III)	(II)–(IV)	(V)–(VI)
(4)	71·6	87·5	89·1	89·6	88·1	6·3
(5)	70·2	89·4	88·1	89·6	88·2	3·8

are equivalent, as expected for the base of a square pyramid, while [Au(biq)Cl_3] has two long and one short Au–Cl bond as would be expected for a trigonal pyramid with its axis through Cl(1), Au, and Cl(3). Thus (4) and (5) are described as a distorted trigonal pyramid, or as being intermediate between trigonal and square pyramidal.[3] From the three five-co-ordinate complexes, it seems possible that a more regular trigonal bipyramid might result from removal of the steric strain from one side of the ligand, *e.g.* removal of the methyl group near N(2) in dmp or the corresponding benzene fragment in biq. However, it is not certain *a priori* that such complexes will still be five-co-ordinate.

[4/1656 *Received*, 1*st August*, 1974]