Characterisation of Two-, Three-, and Four-co-ordinate Gold(I) Complexes by ^{197}Au Mössbauer and ^{31}P-{^{1}H} Nuclear Magnetic Resonance Spectroscopy

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The isolation of some new three- and four-co-ordinate gold(I) complexes is reported. ^{197}Au Mössbauer data are given for two-, three-, and four-co-ordinate complexes, and the technique is shown to be well suited to the determination of co-ordination numbers. For the two- and three-co-ordinate systems the point-charge (partial quadrupole splitting) approach works well, provided that the structures are regular. ^{31}P-{^{1}H} n.m.r. data for the Au^{+}–$P(C_6H_{11})Ph_2$ system show that a maximum of three ligands can be bound to the cation. Data for this and other ligands are correlated with the ligand cone angles. Inconsistencies between the species present in solution and those obtained by crystallisation are discussed.

GOLD(I) most commonly exhibits a co-ordination number of two, but in recent years increasing evidence has been obtained for three- and even four-co-ordination. The known examples, together with the methods of characterisation, are given in Table 1. Two major methods have been employed to establish an expansion of the co-ordination shell. The most generally useful is ^{197}Au Mössbauer spectroscopy, which is being increasingly applied to the characterisation of solid complexes with a wide variety of ligands.[1-6] For complexes containing phosphine ligands, low-temperature ^{31}P n.m.r. spectroscopy is a useful probe of structure in solution.[7-10] We now give further examples of the application of both techniques to the characterisation of gold(I) complexes. Some of the data have been presented in a preliminary communication.[11]

TABLE 1

Three- and four-co-ordinate gold(I) complexes

Complex	Method of characterisation [a]	Ref.
(*a*) Three-co-ordinate		
$[Au(PPh_3)_3][ClO_4]$	M	1
$[Au(PPh_3)_3][B_9H_{12}S]$	X	*b*
$[Au\{P(C_6H_4Me\text{-}p)_3\}_3]^+$	N	9, 10
$[Au(PBu_3)_3]^+$	N	8
$[Au(PMe_2Ph)_3]^+$	N	8
$[Au(PMePh_2)_3]^+$	N	8
$[Au(PEt_3)_3]^+$	N	7
$[Au\{P(OEt)_3\}_3]^+$	N	7
$[Au\{P(OCH_2)_3CEt\}_3]^+$	U	*c*
$[AuCl(PPh_3)_2]$	M, X	3, 5, 17
$[AuI(PPh_3)_2]$	M	3
$[Au(SCN)(PPh_3)_2]$	M	3
$[Au(SnCl_3)(PMe_2Ph)_2]$	M, X	3, 22
$[Au(bipy)(PPh_3)][PF_6]$	M, X	3, 18
$[Au(bipy)(PEt_3)][PF_6]$	M	3
$[Au(phen)(PPh_3)][PF_6]$	M	3
(*b*) Four-co-ordinate		
$[Au(PPh_3)_4][ClO_4]$	M	1
$[Au(PPh_3)_4][BPh_4]$	X	19
$[Au(PMePh_2)_4]^+$	N	8
$[Au(PEt_3)_n\{P(OEt)_3\}_{4-n}]^+$ (n = 0—4)	N	7
$[Au\{P(OCH_2)_3CEt\}_4]]^+$	U	*c*
$[Au\{P(OR)_nPh_{3-n}\}_4]^+$ (R = Me or Et; n = 1 or 2)	A	*d*
$[Au(PMe_3)_4][BF_4]$	A	14
$[Au(pdma)_2][Au(C_6F_5)]$ [e]	X	*f*

[a] A = Chemical analysis, M = ^{197}Au Mössbauer spectroscopy, N = ^{31}P n.m.r. spectroscopy, U = u.v. spectroscopy, X = *X*-ray crystallography. [b] F. Klanberg, E. L. Muetterties, and L. J. Guggenberger, *Inorg. Chem.*, 1968, **7**, 2272. [c] G. P. Fenske and W. R. Mason, *Inorg. Chem.*, 1974, **13**, 1783. [d] D. A. Couch and S. D. Robinson, *Inorg. Chem.*, 1974, **13**, 456. [e] pdma = $C_6H_4(AsMe_2)_2$-*o*. [f] R. Uson, A. Laguna, J. Vicente, J. Garcia, P. G. Jones, and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1981, 655.

EXPERIMENTAL

Gold(I) complexes of the type $[AuCl(L)]$ and $[AuL_2][ClO_4]$ were prepared by routes similar to those described previously.[12] Gold-197 Mössbauer spectra were obtained with source (stationary) and sample (moving) immersed in liquid helium in a Harwell MHC200 cryostat in conjunction with a Harwell series 6000 spectrometer and an Ortec HpGe LEPS detector set on the 77.34 keV † gamma line. The source was obtained by irradiation of ^{196}Pt (75 mg) in the Liverpool and Manchester Universities' Research Reactor at a flux of *ca.* 3×10^{12} n cm^{-2} s^{-1} for 3—8 h. Velocity calibration was with iron foil and a ^{57}Co source, both at room temperature. Isomer shifts are relative to gold foil at 4.2 K. Phosphorus-31 n.m.r. spectra were obtained with a Bruker WP80 spectrometer, with ^{1}H decoupling. Analytical data were provided by the Microanalytical Laboratory of this Department; error limits on phosphorus analyses are *ca.* 0.3%.

Tetrakis(methyldiphenylphosphine)gold(I) *Perchlorate.*—Methyldiphenylphosphine (0.27 cm^3, 1.25 mmol) was added to a solution of $[Au(PMePh_2)_2][ClO_4]$ (0.38 g, 0.54 mmol) in CH_2Cl_2 (25 cm^3). The volume was reduced to 10 cm^3 and toluene (20 cm^3) was added dropwise. Crystals of the *complex* were formed on standing, which were washed with diethyl ether and dried. Yield, 0.49 g (82%) (Found: C, 57.0; H, 4.5; Cl, 11.2; P, 3.5. Calc. for $C_{52}H_{52}AuClO_4P_4$: C, 56.9; H, 4.8; Cl, 11.3; P, 3.2%).

When a mixture of $[AuCl(PMePh_2)]$ (0.543 g, 1.26 mmol) in EtOH (40 cm^3) and $Ag[ClO_4]$ (0.26 g, 1.25 mmol) in EtOH (15 cm^3) was treated, after removal of AgCl, with $PMePh_2$ (0.502 g, 2.50 mmol), a white precipitate was immediately formed, the i.r. spectrum of which showed the product to be a mixture. The solid was redissolved in CH_2Cl_2, toluene was added, and the mixture concentrated to yield three fractions, the first two of which were the bis-ligand complex (Found: C, 45.2, 46.0; H, 3.5, 3.4. Calc. for

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† Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.

$C_{26}H_{26}AuClO_4P_2$: C, 44.8; H, 3.7%); the final crop was the tetrakis complex, $[Au(PMePh_2)_4][ClO_4]$ (Found: C, 58.4; H, 4.4%; calc. values given above).

When a mixture of $[AuCl(PMePh_2)]$ (0.677 g, 1.56 mmol) in CH_3CN (50 cm^3) and $PMePh_2$ (0.625, 3.12 mmol) in $CHCl_3$ (5 cm^3) was treated with $Ag[NO_3]$ (0.266 g, 1.28 mmol) in EtOH–H_2O (9 : 1, 10 cm^3), and precipitated AgCl had been removed, evaporation gave an oily solid which was recrystallised from CH_2Cl_2–$C_6H_5CH_3$ as described above to give $[Au(PMePh_2)_2][NO_3]$. Yield, 0.753 g (73%) (Found: C, 47.2; H, 3.8; N, 1.9; P, 9.5. Calc. for $C_{26}H_{26}AuNO_3P_2$: C, 47.4; H, 4.0; N, 2.1; P, 9.4%).

*Tris(tri-*p*-tolylphosphine)gold*(I) *Perchlorate.*—A solution of $P(C_6H_4Me\text{-}p)_3$ (0.339 g, 1.10 mmol) in CH_2Cl_2 (5 cm^3) was added to a solution of $[Au\{P(C_6H_4Me\text{-}p)_3\}_2][ClO_4]$ (1.01 g, 1.11 mmol) in CH_2Cl_2 (20 cm^3). Toluene (40 cm^3) was added and the mixture was concentrated until cloudy. Sufficient CH_2Cl_2 was added to just dissolve the precipitate (*ca.* 2 cm^3) and the solution was allowed to stand overnight under nitrogen. White crystals (0.807 g) were obtained which were washed with toluene and diethyl ether. The ^{197}Au Mössbauer spectrum showed this product to be principally $[Au\{P(C_6H_4Me\text{-}p)_3\}_3][ClO_4]$ contaminated with *ca.* 20% of the starting complex, and this was confirmed by analysis (Found: C, 61.2; H, 5.1; Cl, 3.4; P, 7.4%). The solid (0.626 g) in CH_2Cl_2 (25 cm^3) was treated with an excess of $P(C_6H_4Me\text{-}p)_3$ (0.253 g, 0.82 mmol) and the *product* isolated by addition of toluene and slow evaporation. Mössbauer spectroscopy and chemical analysis indicated that the product was the pure tris(phosphine) complex. Yield, 0.40 g (*ca.* 65%) (Found: C, 62.2; H, 5.3; Cl, 3.0; P, 7.4. Calc. for $C_{63}H_{72}AuClO_4P_3$: C, 62.6; H, 5.3; Cl, 2.9; P, 7.7%).

Tetrakis(triphenylarsine)gold(I) *Perchlorate.*—A solution of $AsPh_3$ (0.192 g, 0.63 mmol) in CH_2Cl_2 (5 cm^3) was added to a solution of $[Au(AsPh_3)_2][ClO_4]$ (0.570 g, 0.63 mmol) in CH_2Cl_2 (20 cm^3). A slight precipitate of metallic gold was filtered off, the filtrate was concentrated to 10 cm^3 and toluene (100 cm^3) was added, when white *crystals* were formed, which were washed with diethyl ether and identified as $[Au(AsPh_3)_4][ClO_4]$ (Found: C, 56.5; H, 3.9; Cl, 2.9. Calc. for $C_{72}H_{60}As_4AuClO_4$: C, 56.7; H, 3.9; Cl, 2.3%). Concentration of the liquor to half volume yielded another crop of crystals which proved to be $[Au(AsPh_3)_2][ClO_4]$. Yield, 0.53 g (56%) (Found: C, 47.6; H, 3.3; Cl, 4.5. Calc. for $C_{36}H_{30}As_2AuClO_4$: C, 47.6; H, 3.3; Cl, 3.9%).

'*Tris(triphenylarsine)gold*(I) *Nitrate*'.—To a solution of $[AuCl(AsPh_3)]$ (0.742 g, 1.38 mmol) in CH_3CN (50 cm^3) were added $Ag[NO_3]$ (0.234 g, 1.38 mmol) in EtOH–H_2O (9 : 1, 10 cm^3) and $AsPh_3$ (0.844 g, 2.76 mmol) in CH_2Cl_2 (10 cm^3). After removal of AgCl, the solution was evaporated to dryness and the residue recrystallised from CH_2Cl_2–$C_6H_5CH_3$. The white crystalline product analysed as the tris-ligand complex, but the ^{197}Au Mössbauer spectrum showed it to be a mixture of $[Au(AsPh_3)_2][NO_3]$ and $[Au(AsPh_3)_4][NO_3]$. Yield, 0.68 g (42%) (Found: C, 55.4; H, 3.9; N, 1.3. Calc. for $C_{54}H_{45}As_3AuNO_3$: C, 55.1; H, 3.9; N, 1.2%).

RESULTS AND DISCUSSION

Syntheses.—Several complexes of the type $[AuL_2][ClO_4]$ were prepared by methods similar to those used previously,[12] and their reactions with additional free ligand were investigated. For L = $P(C_6H_{11})_3$ (C_6H_{11} = cyclohexyl), recrystallisation of the complex in the presence of two molar equivalents of the ligand gave only the starting bis(phosphine) complex. This result is in agreement with the ^{31}P n.m.r. investigation which showed that higher complexes were not formed.[8]

The reaction of $[Au(PMePh_2)_2][ClO_4]$ with an excess of the phosphine gave the tetrakis complex, $[Au(PMePh_2)_4][ClO_4]$, in good yield. However, the reaction of $[Au(ClO_4)(PMePh_2)]$ (prepared *in situ*) with two molar equivalents of the phosphine gave an immediate precipitate which appeared from its i.r. spectrum to be a mixture. Fractional crystallisation gave first the bis(phosphine) and then the tetrakis(phosphine) complex. When this experiment was repeated with nitrate as the anion, only the bis(phosphine) complex was obtained, in 73% yield. These results are also in accord with ^{31}P n.m.r. data, which showed that at -120 °C with a 1 : 3 (gold : ligand) mol ratio, appreciable quantities of the bis- and tetrakis-ligand complexes were in equilibrium with the tris-ligand complex.[13] Exchange coalescence of the signals occurred at *ca.* -70 °C. It thus appears that the tris complex is unstable to disproportionation [equation (1)].

$$2\,[AuL_3]^+ \rightleftharpoons [AuL_2]^+ + [AuL_4]^+ \qquad (1)$$

A similar situation was found for triphenylarsine, when treatment of $[Au(AsPh_3)_2][ClO_4]$ with one molar equivalent of the ligand yielded, on fractional crystallisation, first the tetrakis- and then the bis-ligand complex. Treatment of $[Au(NO_3)(AsPh_3)]$ (prepared *in situ*) with two molar equivalents of the ligand gave a single product analysing as the tris complex. The ^{197}Au Mössbauer spectrum, however, showed this product to be a mixture (see below). The cation $[Au(PMe_3)_3]^+$ is also thought to be unstable to disproportionation.[14]

Treatment of $[Au\{P(C_6H_4Me\text{-}p)_3\}_2][ClO_4]$ with one molar equivalent of ligand yielded a mixture of the bis and tris complexes. Addition of an excess of the ligand allowed crystallisation of the tris-ligand complex, but we could not isolate the tetrakis-ligand complex obtained by Muetterties *et al.*[10] with borane anions.

*Gold-*197 *Mössbauer Spectra.*—New data for gold(I) complexes are given in Table 2.

For two-co-ordinate gold(I) systems there is a good correlation between isomer shift (i.s.) and quadrupole splitting (q.s.),[5,6,15,16] to which the new data reported here conform. Both parameters are expected to increase as the donor power of the ligands increases, *e.g.* from halides to cyanide. The correlation shows some curvature,[5] due to changes in hybridisation of the gold atom, and it has been shown [4] that better linearity is displayed if only complexes of a similar type are compared, *e.g.* $[Au(PR_3)L]$ (*cf.* Figure 1). In such a series the hybridisation is less variable.

The parameters found here for $[AuI(PPh_3)]$ agree well with those reported by Vollenbroek *et al.*,[2] and fit the correlation of Figure 1. The data originally reported by Charlton and Nicholls [6] do not fit, showing a lower i.s., and agree better with the data for $[AuI(PPh_3)_2]$.

TABLE 2

^{197}Au Mössbauer data for gold(I) complexes (4.2 K)

	i.s.[a,b] mm s^{-1}	q.s.[b] mm s^{-1}	Γ[c] mm s^{-1}	χ^2/d.f.[d]
(*a*) Two-co-ordinate				
[AuCl(AsMe$_2$Ph)]	2.93	6.37	2.08, 2.15	0.86
[AuBr(PMePh$_2$)]	3.91	7.02	1.96, 1.98	1.05
[AuBr{P(C$_6$H$_{11}$)$_3$}]	4.19	7.56	2.03, 1.97	0.87
[AuI(PPh$_3$)] [e]	4.07	7.36	2.48 [f]	0.76
f	3.98	7.35		
[Au{P(C$_6$H$_4$Me-*p*)$_3$}$_2$]-[ClO$_4$] [g]	5.43	9.64	2.16, 2.14	1.02
[Au{P(C$_6$H$_{11}$)Ph$_2$}$_2$]-[ClO$_4$]	5.36	9.95	2.07, 1.98	1.00
[Au(AsMe$_2$Ph)$_2$][ClO$_4$]	4.08	8.24	1.91, 2.18	1.11
(*b*) Three-co-ordinate				
[AuI(PPh$_3$)$_2$] [e]	2.57	8.08	2.17 [f]	1.05
h	2.66	7.87		
[Au{P(C$_6$H$_4$Me-*p*)$_3$}$_3$]-[ClO$_4$]	2.99	9.74	2.00, 2.14	1.04
'[Au(AsPh$_3$)$_3$][NO$_3$]' [i]	3.25	7.38	2.21, 2.76 [j]	0.96
(*c*) Four-co-ordinate				
[Au(PMePh$_2$)$_4$][ClO$_4$]	1.48	0.00	2.13	0.93
[Au(AsPh$_3$)$_4$][ClO$_4$]	−0.39	0.00	2.12	0.97

[a] Relative to gold foil. [b] ±0.05 mm s^{-1}. [c] ±0.08 mm s^{-1}. [d] d.f. = Degrees of freedom. [e] These data were obtained in collaboration with Dr. J. D. Rush. [f] Widths held equal. [g] Ref. 2. [h] Ref. 3. [i] This material is a mixture (see text). [j] ±0.25 mm s^{-1}.

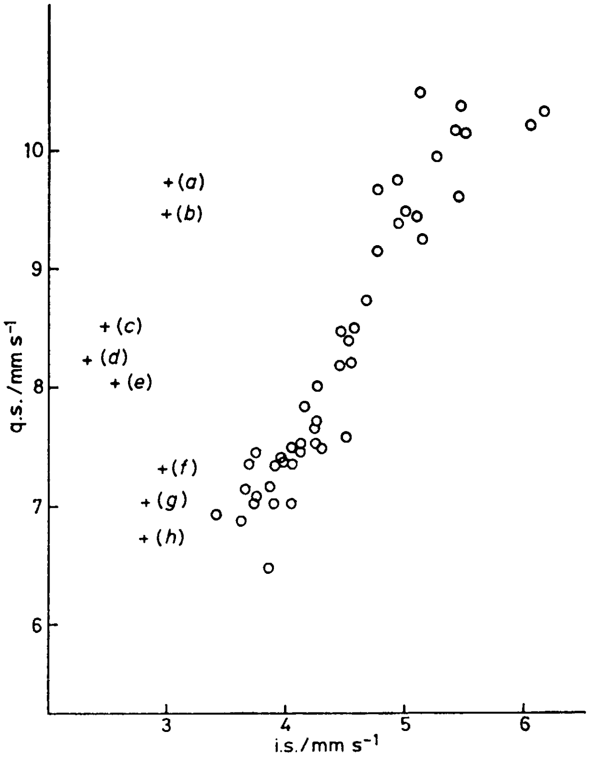

FIGURE 1 ^{197}Au Mössbauer data for gold(I)–phosphine complexes. Two-co-ordinate complexes (O) (data from Table 2, refs. 1, 4—6, and H. Schmidbauer, J. R. Mandl, F. E. Wagner, D. F. von der Vondel, and G. P. van der Kelen, *J. Chem. Soc., Chem. Commun.*, 1976, 170). Three-co-ordinate complexes (+): [Au{P(C$_6$H$_4$Me-*p*)$_3$}$_3$][ClO$_4$] (*a*); [Au(PPh$_3$)$_3$][ClO$_4$] (*b*); [Au(SCN)(PPh$_3$)$_2$] (*c*); [AuCl(PPh$_3$)$_2$] (*d*); [AuI(PPh$_3$)$_2$] (*e*); [Au(bipy)(PEt$_3$)][PF$_6$] (*f*); [Au(phen)(PPh$_3$)][PF$_6$] (*g*); [Au(bipy)(PPh$_3$)][PF$_6$] (*h*) (from Table 2, refs. 1, 3)

Similarly, the values reported by Jones *et al.*[4] for [Au(SCN)(PPh$_3$)] agree closely with those for [Au(SCN)(PPh$_3$)$_2$].[3]

Data for three-co-ordinate complexes are also shown in Figure 1. All lie to the low-i.s. side of the band of values for two-co-ordinate systems. The q.s. values span a considerable range, but the i.s. are less variable, 2.3—3.0 mm s^{-1}. It might be expected that three-co-ordinate complexes would show an i.s.–q.s. correlation similar to that for the two-co-ordinate complexes, and this point is discussed further below. As pointed out previously,[1] the q.s. of comparable two- and three-co-ordinate complexes are expected to be similar, so that the change in co-ordination number is manifested primarily as a decrease in i.s. A further substantial decrease is observed when a fourth ligand is bound, but in this case the q.s. also decreases sharply, to zero in [AuL$_4$]$^+$. The decrease in i.s. with increasing co-ordination number is due principally to the change in hybridisation from *sp* to *sp*^{2} to *sp*^{3}. The *s* character per bond decreases and the total *p*-electron density increases, both of which features would decrease the electron density at the nucleus. An additional factor is the increase in bond distance with increasing co-ordination number. As shown in Table 3, for phosphine complexes the average Au–P distance is 228 pm for two-co-ordination, 239 pm for three-co-ordination, and 257 pm for four-co-ordination. This increase reflects and reinforces the increase in *p* character, and is consistent with the reduction in i.s.

TABLE 3

Gold(I)–phosphorus bond lengths

	d(Au–P)/pm	Ref.
(*a*) Two-co-ordinate		
[AuCl(PPh$_3$)]	224.3	*a*
[Au(CN)(PPh$_3$)]	227	*b*
[Au(CH$_3$)(PPh$_3$)]	227.9	*c*
[Au(C$_6$F$_5$)(PPh$_3$)]	227	*d*
[(Ph$_3$P)AuC(CF$_3$)=C(CF$_3$)Au(PPh$_3$)]	228	*e*
[ClAuP(Ph$_2$)CH$_2$P(Ph$_2$)AuCl]	223.8	*f*
[Au{P(C$_6$H$_{11}$)$_3$}$_2$][SCN]	230, 231	*g*
[Au(PMePh$_2$)$_2$][PF$_6$]	231.6	*h*
(*b*) Three-co-ordinate		
[AuCl(PPh$_3$)$_2$]·0.5C$_6$H$_6$	232.4, 233.9	17
[Au(PPh$_3$)$_3$][B$_9$H$_{12}$S]	238.2	*i*
[Au(PPh$_3$)$_3$][BPh$_4$] [j]	243.4, 244.5, 246.1	19
j, k	235.9, 238.9, 240.1	19
[Au(PPh$_3$)$_3$][BPh$_4$]·PPh$_3$	239.2, 240.6, 240.8	19
(*c*) Four-co-ordinate		
[Au(PPh$_3$)$_4$][BPh$_4$]	260.2, 261.0	19
k	250.4, 256.1	19

[a] N.C. Baenziger, W. E. Bennett, and D. M. Soboroff, *Acta Crystallogr., Sect. B*, 1976, **32**, 692. [b] P. L. Bellon, M. Manassero, and M. Sansoni, *Ric. Sci.*, 1969, **39**, 173. [c] P. D. Gavens, J. J. Guy, M. J. Mays, and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 1977, **33**, 136. [d] R. W. Baker and P. J. Pauling, *J. Chem. Soc., Dalton Trans.*, 1972, 2264. [e] C. J. Gilmore and P. Woodward, *Chem. Commun.*, 1971, 1233. [f] H. Schmidbauer, A. Wohlleben, F. Wagner, O. Orama, and G. Huttner, *Chem. Ber.*, 1977, **110**, 1748. [g] J. A. Muir, M. M. Muir, and E. Lorca, *Acta Crystallogr., Sect. B*, 1980, **36**, 931. [h] J. J. Guy, P. G. Jones, and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 1976, **32**, 1973. [i] L. J. Guggenberger, *J. Organomet. Chem.*, 1974, **81**, 271. [j] In [Au(PPh$_3$)$_4$][BPh$_4$]. [k] At −150 °C.

In two cases, strict comparison can be made of the q.s. for two- and three-co-ordination. For the complexes of $P(C_6H_4Me\text{-}p)_3$, the q.s. is the same within experimental error (9.64 and 9.74 mm s^{-1}), as had previously been found for the PPh_3 complexes (9.51 and 9.47 mm s^{-1}).[1,4,5] On the point-charge or molecular-orbital treatments,[1] the q.s. values are expected to be the same, if the usual assumption is made that the extent of donation of charge by a ligand is independent of the co-ordination number of the metal. Other workers anticipated a smaller q.s. for the three-co-ordinate system.[3]

The agreement with the predictions of the point-charge model suggests that the partial quadrupole splitting (p.q.s.) approach might be usefully applied. For $[AuL_3]^+$ the calculated q.s. is -3 p.q.s. ^{3}(L), where ^{3}(L) represents the value for ligand L in a three-co-ordinate system. Similarly, the calculated q.s. for $[AuL_2]^+$ is $+4$ p.q.s. ^{2}(L). Thus, the calculated ratio of p.q.s. values, $^3L : {}^2L$, is 1.33; for $L = P(C_6H_4Me\text{-}p)_3$ and PPh_3, the observed ratio is 1.35. Further direct checks of the additivity model are highly desirable, and should be made as soon as data for suitable pairs of compounds become available. Meanwhile, indirect checking can be carried out by deriving calculated q.s. values for three-co-ordinate mixed-ligand complexes, for several of which experimental data are available. Thus, we have used q.s. data for two-co-ordinate complexes to derive p.q.s. ^{2}(L), which we have converted to ^{3}L values using the relationship: 12 p.q.s. ^{2}(L) = 9 p.q.s. ^{3}(L) = 8 p.q.s. ^{4}(L). (The numerical factors are derived from the *p* character of *sp*, *sp*^{2}, and *sp*^{3} hybrids: $\frac{1}{2}$, $\frac{2}{3}$, and $\frac{3}{4}$ respectively.) The derived p.q.s. ^{3}(L) values (Table 4) were used to calculate the q.s. for several three-co-ordinate complexes, and comparison with the observed values is made in Table 5. Agreement is excellent for the phosphine complexes, being well within the experimental error (usually quoted as 0.05—0.10 mm s^{-1}), and includes $[AuCl(PPh_3)_2]$ which has a distorted structure.[17] The calculated q.s. is, of course, independent of the L–Au–L bond angles, provided only that the gold atom is coplanar with the three ligands. Agreement is less good for the complexes containing bipyridyl (bipy) or phenanthroline (phen). The p.q.s. values for these ligands were estimated from analogous pyridine (py) complexes, so the disagreement may simply mean that pyridine is not a good model. However, in the complex $[Au(bipy)(PPh_3)][PF_6]$, the gold atom shows a very irregular co-ordination.[18] The AuN_2P unit is almost planar but the two Au–N distances are significantly different, 217 and 241 pm. The short Au–N bond makes an angle of 157° with the Au–P bond, so that the structure is intermediate between three- and two-co-ordination. The Au–P bond length is actually shorter than those in many two-co-ordinate systems (212 pm, *cf.* Table 3). These distortions, by reducing the extent of donation from one nitrogen atom, would certainly lower the q.s. below the value calculated for regular trigonal co-ordination (as observed). It is also probable that the i.s. would be rather greater than for regular three-co-ordination. Thus, the data for the AuN_2P complexes lie closer to the values expected for two-co-ordination (*cf.* Figure 1) than they would for regular trigonal co-ordination. It therefore seems likely that regular three-co-ordinate systems will give a band of values similar to that for two-co-ordination, but with a more positive slope.

TABLE 4

Partial quadrupole splitting parameters for two- and three-co-ordination

L	Estimator	q.s.[a] mm s^{-1}	p.q.s./mm s^{-1} ^{2}L [b]	p.q.s./mm s^{-1} ^{3}L [c]
PPh_3	$[Au(PPh_3)_2][ClO_4]$	9.51	−2.38	−3.17
$P(C_6H_{11})_3$	$[Au\{P(C_6H_{11})_3\}_2][ClO_4]$	9.64	−2.41	−3.21
Cl^-	$[AuCl(PPh_3)]$	7.45	−1.35	−1.79
I^-	$[AuI(PPh_3)]$	7.36	−1.34	−1.79
SCN^-	$[Au(SCN)(PPh_3)]$	7.65	−1.43	−1.91
py	$[Au(py)(PPh_3)][PF_6]$	8.50	−1.82	−2.43
PEt_3	$[Au(PEt_3)_2][PF_6]$	10.18	−2.54	−3.39

[a] Average of available data. [b] Calculated assuming $V_{zz} < 0$. [c] Derived with the assumption that p.q.s. ^{3}(L) = 1.33 p.q.s. ^{2}(L) (see text).

TABLE 5

Calculated and observed quadrupole splittings

Complex	q.s. (calc.) mm s^{-1}	q.s. (obs.) mm s^{-1}	q.s. (obs.) − q.s. (calc.) mm s^{-1}
$[Au(PPh_3)_3][ClO_4]$	+9.51	9.47	−0.04
$[Au\{P(C_6H_{11})_3\}_3][ClO_4]$	+9.63	9.74	+0.11
$[AuCl(PPh_3)_2]$	+8.13	8.22	+0.09
$[AuI(PPh_3)_2]$	+8.13	7.97	−0.16
$[Au(SCN)(PPh_3)_2]$	+8.25	8.52	−0.27
$[Au(py)_2(PPh_3)]^+$	+8.03	6.67 [a]	−1.36
		7.05 [b]	−0.98
$[Au(py)_2(PEt_3)]^+$	+8.25	7.33 [c]	−0.92

[a] Value for $[Au(bipy)(PPh_3)][PF_6]$. [b] Value for $[Au(phen)(PPh_3)][PF_6]$. [c] Value for $[Au(bipy)(PEt_3)][PF_6]$.

Four-co-ordinate complexes of the type $[AuL_4]^+$ are readily recognised by the zero q.s. required by T_d symmetry. It has been suggested that for $[Au(PPh_3)_4][BPh_4]$ four-co-ordination is less favourable than three-co-ordination, and requires low temperatures for its attainment.[19] *X*-Ray data show that at 123 K one-seventh of the cations have a distorted trigonal structure with one long Au–P bond. At higher temperatures the proportion of distorted cations increases. The Mössbauer data gave no indication of a second component but this would, in any case, be of very low intensity.

Only one mixed-ligand four-co-ordinate species has been examined by Mössbauer spectroscopy, $[Au(SnCl_3)(PPh_3)_3]$.[3] The low values of i.s. and q.s. in the ^{197}Au spectrum (1.64, 3.57 mm s^{-1}) both indicate considerable interaction between the gold and tin atoms, and rule out the ionic formulation $[Au(PPh_3)_3][SnCl_3]$. The ^{119}Sn Mössbauer parameters [i.s.(SnO_2) 2.44, q.s. 1.58 mm s^{-1}] are also consistent with such interaction.[20] This situation contrasts with that for the compound $Au(SnCl_3)(PMe_2Ph)_2$, for which the ^{119}Sn data (i.s. 2.92, q.s. 1.35 mm s^{-1}) suggest that the Au–Sn interaction is weak.[21] The ^{197}Au Mössbauer data were originally interpreted as supporting a three-co-ordinate structure,[3] but the parameters fit well into the two-co-ordination band of Figure 1 (i.s. 4.18, q.s. 8.39 mm s^{-1}). *X*-Ray data reveal a structure similar to that in [Au(bipy)(PPh_3)][PF_6]: an essentially planar $AuSnP_2$ unit, a large P–Au–P bond angle (154°), and a long Au–Sn bond (288 pm).[22] Thus, the crystal structure is consistent with some donation from tin to gold, but the Mössbauer data are close to those expected for an ionic structure. It is therefore interesting to compare the two Au–$SnCl_3$ complexes by the point-charge method. From the data of Table 4, p.q.s. ^{4}(PPh_3) may be calculated, from which values of ^{4}($SnCl_3^-$) and hence ^{3}($SnCl_3^-$) can be obtained (Table 6). P.q.s. values for ^{2}(PMe_2Ph) and ^{3}(PMe_2Ph) can also be derived, whence the calculated q.s. for [Au($SnCl_3$)(PMe_2Ph)$_2$] is (+)8.06 mm s^{-1}; the observed value is 8.39 mm s^{-1}. Such reasonable agreement is probably best interpreted as meaning that the Au–Sn bond in the four-co-ordinate complex is also elongated, in a similar way to that found for one Au–P bond in [Au(PPh_3)$_4$][BPh_4].[19]

TABLE 6

P.q.s. values for $SnCl_3^-$ and $PMePh_2$

L	Estimator	q.s. mm s^{-1}	p.q.s./mm s^{-1} ^{2}L	^{3}L *	^{4}L *
PPh_3	[Au(PPh_3)$_2$][ClO_4]			−3.17	*−3.56*
$SnCl_3^-$	[Au($SnCl_3$)(PPh_3)$_3$]	3.57		*−1.58*	−1.77
PMe_2Ph	[Au(PMe_2Ph)$_2$]Cl	9.26	−2.32	*−3.24*	
	[Au(PMe_2Ph)$_2$][PF_6]	10.15	−2.54		

$$\begin{aligned}\text{q.s.}\{[\text{Au}(\text{SnCl}_3)(\text{PMe}_2\text{Ph})_2]\} &= -\ \text{p.q.s.}\ {}^3(\text{SnCl}_3^-)\\ &\quad -\ 2\ \text{p.q.s.}\ {}^3(\text{PMe}_2\text{Ph})\\ &= +8.06\ \text{mm s}^{-1}\end{aligned}$$

* Values in italics are derived from those in Roman type.

One further illustration can be given of the utility of ^{197}Au Mössbauer data in the characterisation of gold(I) complexes. During attempts to obtain additional examples of high co-ordination numbers, a compound analysing as [Au($AsPh_3$)$_3$][NO_3] was isolated (see above). Its Mössbauer spectrum was an asymmetric doublet with peak intensities *ca.* 3 : 1, that at lower velocity being the more intense. Compared to those for the three-co-ordinate systems described above, the i.s. seems rather high relative to the q.s. The parameters fit the two-co-ordination correlation of Figure 1, and agree very well with those of other two-co-ordinate gold(I) arsine complexes (Figure 2). The position of the more intense, low-velocity peak corresponds closely to that of the single peak of [Au($AsPh_3$)$_4$][ClO_4]. It thus appears that the solid contains equal amounts of the bis- and tetrakis-triphenylarsine complexes. It is unlikely that such a diagnosis could have been easily made by other methods.

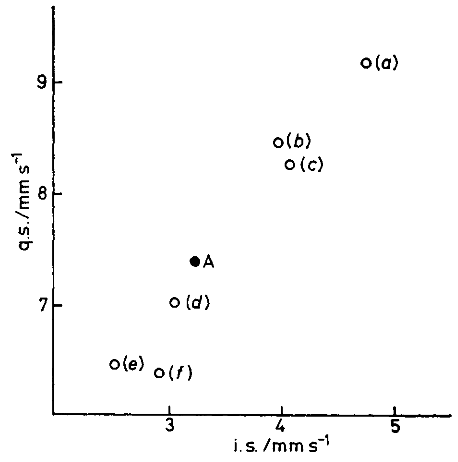

FIGURE 2 ^{197}Au Mössbauer data for gold(I)–arsine complexes: [Au($AsPh_3$)(PPh_3)][PF_6] (*a*); [Au($AsPh_3$)$_2$][ClO_4] (*b*); [Au($AsMe_2Ph$)$_2$][ClO_4] (*c*); [AuCl($AsPh_3$)] (*d*); [ClAuAs(Me_2)-CH=CHAs(Me_2)AuCl] (*e*); [AuCl($AsMePh_2$)] (*f*). Point A represents '[Au($AsPh_3$)$_3$][NO_3]' (data from Table 2, refs. 4—6)

Phosphorus-31 *N.M.R. Spectra*.—The ^{31}P-{^{1}H} n.m.r. spectrum of [Au{P(C_6H_{11})Ph_2}$_2$][ClO_4] was obtained at various temperatures and in the presence of various amounts of added ligand. The data are summarised in Table 7. At ambient temperature, sharp signals are seen which move progressively to higher field as increasing amounts of ligand are added. On cooling to 180 K, the spectrum of the pure complex showed no change, but all the other systems gave two well resolved, sharp signals. Thus, only two species are present in any one mixture, either [AuL_2]$^+$ and [AuL_3]$^+$, or [AuL_3]$^+$ and free L, depending on the stoicheiometry [L = P(C_6H_{11})Ph_2]. No signals corresponding to [AuL_4]$^+$ were seen. The intensities (roughly proportional to integrated areas) agreed with those expected from the stoicheiometry. When the mixtures were warmed, the spectra broadened, coalesced, and finally gave sharp signals the positions of which correspond to the calculated weighted averages: [AuL_2]$^+$ + [AuL_3]$^+$, 47.6 p.p.m. (observed, 46.9 p.p.m.); [AuL_3]$^+$ + L, 31.5 p.p.m. (observed, 32.0 p.p.m.). This observation confirms that only two species are present in each mixture, and indicates that the complexes do not dissociate appreciably at room temperature, *i.e.* that equilibrium (2) is rapid and has a

TABLE 7

^{31}P-{^{1}H} n.m.r. data for CH_2Cl_2 solutions of [AuL_2][ClO_4] with added L [L = P(C_6H_{11})Ph_2]

	T/K	δ/p.p.m.*	Assignment
[AuL_2][ClO_4]	310	54.3	[AuL_2]$^+$
	200	54.0	[AuL_2]$^+$
[AuL_2][ClO_4] +0.5 L	310	46.9	Rapid exchange
	200	*ca.* 53.0 (vbr)	[AuL_2]$^+$
		ca. 48.9 (vbr)	[AuL_3]$^+$
	180	53.9 (79)	[AuL_2]$^+$
		47.1 (106)	[AuL_3]$^+$
[AuL_2][ClO_4] +1.0 L	310	43.2 (br)	Rapid exchange
	180	53.5 (vw)	[AuL_2]$^+$, trace
		48.5	[AuL_3]$^+$
[AuL_2][ClO_4] +1.5 L	310	*ca.* 32.0	Rapid exchange
	180	48.5 (142)	[AuL_3]$^+$
		−7.7 (18)	L
[AuL_2][ClO_4] +2.0 L	310	*ca.* 32.0	Rapid exchange
	180	48.5 (86)	[AuL_3]$^+$
		−7.6 (26)	L
L	310	−3.7	
	200	−7.0	

* Chemical shifts downfield from 85% H_3PO_4, vbr = very broad, vw = very weak, figures in parentheses are intensities.

large equilibrium constant. Exchange between $[AuL_3]^+$ and $[AuL_2]^+$ must proceed by dissociation of $[AuL_3]^+$, but the liberated ligand is rebound very rapidly. It is not possible to deduce from the data available whether exchange between $[AuL_3]^+$ and L is associative or dissociative, although the former seems more likely. The

$$[AuL_2]^+ + L \rightleftharpoons [AuL_3]^+ \qquad (2)$$

resonances move to higher field, toward the free-ligand value, as the co-ordination number increases. Similar trends are found for complexes of silver(I), palladium(0), and platinum(0) (Table 8).

TABLE 8

^{31}P co-ordination chemical shifts, δ(complex) − δ(ligand)

M	L	$[ML_2]$	$[ML_3]$	$[ML_4]$	T/K	Solvent	Cone angle (°)	Ref.
Au^+	$P(C_6H_{11})Ph_2$	61.6 [a]	56.2 [a]		180	CD_2Cl_2	154	
	$P(C_6H_{11})_3$	54.3			193	CH_2Cl_2	170	8
	PBu^n_3	73.5	70.3		193	CH_2Cl_2	132	8
	PMe_2Ph	62.1	24.2	$\leqslant 11.8$ [b]	193	CH_2Cl_2	136	8
	$PMePh_2$	54.5	42.3	22.8	193	CH_2Cl_2	136	8
	$P(C_6H_4Me\text{-}p)_3$	52.2	50.3	47 [b]	189	CH_2Cl_2	145	9, 10
	PEt_3	62.4	57.4	13.4	175	CH_2Cl_2	133	7
Ag^+	$P(C_6H_4Me\text{-}p)_3$	22.0	19.5	14.5	193	CH_2Cl_2	145	9, *c*
Pt^0	PEt_3		64.0	4.6	199	$C_6H_5CH_3$	133	24
	PBu^n_3		65.6	7.7	199	$C_6H_5CH_3$	132	24
	PPr^i_3	70.7	64.4		199	$C_6H_5CH_3$		24
	$P(C_6H_{11})_3$	53.6	45.0		199	$C_6H_5CH_3$	170	24
	PBu^t_2Ph	48.3			199	$C_6H_5CH_3$		24
Pd^0	PEt_3		9.6	−1.5	213	$C_6H_5CH_3$	133	24
	PBu^n_3		−1.4	−7.9	173	$C_6H_5CH_3$	132	24
	PPr^i_3	49.3	38.0		193	$C_6H_5CH_3$		24
	$P(C_6H_{11})_3$	38.7	25.9		213	$C_6H_5CH_3$	170	24
	PBu^t_2Ph	67.0			213	$C_6H_5CH_3$		24

[a] Derived using an extrapolated value of −7.6 p.p.m. for the chemical shift of $P(C_6H_{11})Ph_2$ at 180 K. [b] May be a rapidly exchanging mixture of $[AuL_3]^+$ and L. [c] E. L. Muetterties and C. W. Alegranti, *J. Am. Chem. Soc.*, 1972, **94**, 6386.

With the majority of ligands, co-ordination numbers up to four are observed with each of the metals. However, with the bulkiest ligands the co-ordination number is limited by steric effects. For gold(I) and $P(C_6H_{11})Ph_2$, only two- and three-co-ordination are found, and with $P(C_6H_{11})_3$ only two ligands can be bound. These trends reflect the cone angles of the ligands.[23] Similar behaviour is observed for palladium(0) and platinum(0), except that at low temperatures these metals achieve three-co-ordination even with $P(C_6H_{11})_3$.[24] It is unlikely that neutral atoms would be more effective acceptors than gold(I), and the greater tendency to three-co-ordination is presumably due to the larger radii of the neutral atoms.

Conclusion.—The co-ordination number of gold(I) in solid materials can readily be determined by the Mössbauer method. The i.s. and q.s. taken together are diagnostic, at least for systems with regular geometry. In solution, ^{31}P n.m.r. spectroscopy is a useful tool, but a single measurement does not give a unique identification of the species present. As shown in Table 8, a wide variety of chemical shifts is seen, with different ranges for different ligands, and it would be necessary to observe all the possible species before any one could be positively identified from its chemical shift alone.

From a comparison of the two sets of data, it is apparent that, for many ligands, more species are capable of existence in solution than can be crystallised from the solution. For instance, for L = PEt_3, all the complexes $[AuL_n]^+$ (n = 2, 3, or 4) [7] could be observed in solution, but Mays and Vergnano were able to crystallise only $[Au(PEt_3)_2][PF_6]$ even in the presence of a five-fold molar excess of the ligand. Similarly, for L = $PMePh_2$, we were able to isolate only $[Au(PMePh_2)_2][NO_3]$ from solutions with a 3 : 1 mol ratio of L : Au. However, with ClO_4^- as counter ion and the same L : Au ratio, the solids isolated were the bis- and tetrakis-ligand complexes, which crystallised separately. A similar disproportionation occurred for L = $AsPh_3$ with NO_3^- or ClO_4^- as counter ion.

Muetterties and co-workers [9,10] observed $[AuL_2]^+$ and $[AuL_3]^+$ in solution for L = $P(C_6H_4Me\text{-}p)_3$, but could not find unequivocal evidence for $[AuL_4]^+$. With ClO_4^- as counter ion, we were able to isolate both the bis- and tris-ligand cations, and the latter was obtained also in the presence of an excess of the ligand. However, Muetterties *et al.* found that with $B_9H_{12}S^-$ all three cations $[AuL_n]^+$ (n = 2, 3, or 4) could be isolated, but with $B_9H_{14}^-$, $B_{10}H_{15}^-$, or $B_{11}H_{14}^-$ only $[AuL_4]^+$ was obtained.

Thus, although several species may be present in solution, the salts crystallised out do not necessarily correspond to the major species. The trend here is the usual one,[25] *viz.* that small anions favour the isolation of the smaller bis-ligand cations, and larger anions favour the larger tetrakis-ligand cations. The various factors at work are clearly very delicately balanced, however. For instance, for L = $P(C_6H_4Me\text{-}p)_3$, only the bis and tris complexes can be isolated with ClO_4^- as counter ion, but all three cations can be obtained with the larger anion $B_9H_{12}S^-$. Still larger anions yield only the tetrakis cation.[10] With L = PPh_3, the cations are slightly smaller, and all three cations can be readily crystallised as perchlorates.[1,26] For L = $PMePh_2$ or $AsPh_3$, the situation is further complicated by the disproportionation of the tris complex.

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