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Structure and Bonding in Gold(I) Compounds. Part 3.† Mössbauer Spectra of Three-co-ordinate Complexes

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Mössbauer spectra are reported for a number of gold(I) complexes which might be expected to be three-co-ordinate. The spectral data are related to the possible electronic and geometric structures of these complexes. It is shown that the Mössbauer spectrum provides a useful, although not invariably unambiguous, indication of geometry.

SEVERAL complexes of Au^I with co-ordination numbers of three or four have now been characterised by *X*-ray diffraction.[1–3] This has thrown doubt on the previous assignment of complexes of the type $[AuL_2X]$ and $[AuLL'X]$ (L, L′ are two-electron donors and X is an anionic species) as ionic in the solid state. When either L or L′ has more than one donor site, or when X may co-ordinate to the metal, a co-ordination number of greater than two is quite possible. Vibrational spectra are of little use in resolving this uncertainty as, for example, the three-co-ordinate[1] $[AuCl(PPh_3)_2]$ shows no i.r.-stretching frequency in the solid state[4] and has a similar Raman spectrum to $[Au(PPh_3)_2][PF_6]$, presumed to be two-co-ordinate.

The purpose of this paper is to discuss the effect on the ^{197}Au Mössbauer parameters of these complexes of the variation of co-ordination, and, if possible, establish a correlation between spectra and structures which may be used to predict the co-ordination in such complexes.

EXPERIMENTAL

Mössbauer spectra were obtained with source and absorber at liquid-helium temperature as described in the previous paper.[5] The following complexes were prepared by literature methods: $Au(PPh_3)_2X$ (X = Cl,[6] I,[4] SCN,[7] or PF_6 [5]), $[Au(PEt_3)_2][PF_6]$,[5] $[Au(PPh_3)L][PF_6]$ (L = C_5H_5N, PPh_3S, or PPh_3O),[5] $Au(PMe_2Ph)X$ (X = PF_6 [5] or $SnCl_3$ [8]), $Au(C_5H_{11}N)_2X$ (X = Cl or PF_6),[9] and $Au(etu)_2X$ [etu = ethylenethiourea, X = Cl (monohydrate) [10] or PF_6 [5]].

$[Au(PPh_3)L][PF_6]$ [L = 2,2′-*Bipyridyl* (*bipy*), 1,10-*Phenanthroline* (*phen*), *or* $Et_2P(S)(S)PEt_2$].—The general method was to add a stoicheiometric amount of L and 10% excess of $Ag[PF_6]$ in dichloromethane to a chloroform solution of $[AuCl(PPh_3)]$. The filtered solution was then concentrated *in vacuo*, and crystallisation was induced by addition of diethyl ether.

L = *bipy*. The complex $[AuCl(PPh_3)]$ (0.5 g) gave 0.33 g (43%) of product (Found: C, 43.1; H, 3.0; N, 3.9. $C_{28}H_{23}AuF_6N_2P_2$ requires C, 44.2; H, 3.1; N, 3.7%).

L = *phen*. The complex $[AuCl(PPh_3)]$ (0.25 g) gave 0.295 g (74%) of product (Found: C, 46.0; H, 3.2; N, 3.8; P, 8.2, 8.0. $C_{30}H_{23}AuF_6N_2P_2$ requires C, 45.9; H, 3.0; N, 3.6; P, 7.9%).

L = $Et_2P(S)(S)PEt_2$. The complex $[AuCl(PPh_3)]$ (0.5 g) gave two products (1) and (2). The minor product (1) (90 mg) formed first. After concentration of the solution and addition of more diethyl ether, 0.53 g of (2) precipitated. Complex (2) was the required product (Found: C, 37.1; H, 4.0; P, 15.3. $C_{26}H_{35}AuF_6P_4S_2$ requires C, 36.9; H, 4.2; P, 14.6%). The analysis of (1) is consistent with its formulation as $[AuL_3][PF_6]$ (Found: C, 26.3; H, 5.3; P, 21.0. $C_{24}H_{60}AuF_6P_7S_6$ requires C, 27.0; H, 5.7; P, 20.3%).

$Au(PEt_3)_2X$ (X = Cl *or* I).—To a solution of PEt_3 (0.118 g) in diethyl ether (10 cm^3) was added a solution of the stoicheiometric amount of $[Au(PEt_3)X]$ in dichloromethane (5 cm^3). After 0.5 h of vigorous shaking, the solvent was removed *in vacuo* and the residue was recrystallised from ethanol. X = Cl, yield 0.185 g (40%) (Found: C, 31.1; H, 6.4. $C_{12}H_{30}AuClP_2$ requires C, 30.7; H, 6.4%); X = I, yield 0.492 g (38%) (Found: C, 26.6; H, 5.7. $C_{12}H_{30}AuIP_2$ requires C, 25.7; H, 5.4%).

All the above complexes formed as colourless crystals.

$[Au(bipy)(PEt_3)][PF_6]$.—The complex $[AuCl(PEt_3)]$ (400 mg) in chloroform was treated as above with an excess of 2,2′-bipyridyl and $Ag[PF_6]$ and the solution was filtered. Addition of diethyl ether gave a yellow precipitate containing pale cream crystals (0.53 g, 75%) (Found: C, 32.3; H, 3.7; N, 4.8. $C_{16}H_{23}AuF_6N_2P_2$ requires C, 31.2; H, 3.8; N, 4.6%).

THEORETICAL CORRELATION BETWEEN STRUCTURE AND MÖSSBAUER SPECTRA

In the preceding paper[5] we showed that the best treatment of two-co-ordinate linear gold(I) complexes involved *sp* hybridisation of the gold. The *X*-ray structure determinations available for three-co-ordinate Au^I show approximate trigonal-planar geometry, suggesting an sp^2 hybridisation of the gold. For this geometry the principal axis of the electric-field gradient (e.f.g.) tensor, V_{zz}, will lie perpendicular to the metal–ligand plane and the sign of V_{zz} will be different from that found for the linear gold complexes.

If we assume that the total charge donated to the gold in three-co-ordinate complexes (q) is equally spread between the $6s$, $6p_y$, and $6p_x$ orbitals, then we obtain (1) and (2) using the relations between orbital occupations and electric

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field gradients given by Clark.[11] For two-co-ordinate (*sp* hybridised) Au^I, if a charge q' is donated, then we obtain

$$\text{Isomer shift} \propto \frac{q}{3} + \text{a constant} \quad (1)$$

$$|V_{zz}| \propto 2 \cdot \frac{2}{5} \cdot \frac{q}{3} \quad (2)$$

relations (3) and (4). If the same amount of charge is donated in two- and three-co-ordination ($q = q'$) then we would expect a decrease of *ca.* 33% in the quadrupole

$$\text{Isomer shift} \propto \frac{q'}{2} + \text{a constant} \quad (3)$$

$$|V_{zz}| \propto \frac{4}{5} \cdot \frac{q'}{2} \quad (4)$$

splitting on going from two- to three-co-ordination, and also a decrease in the isomer shift.

It should be noted that, as the isomer shift for a pure Au^+ species is unknown, it is impossible to predict the percentage change in isomer shift. It is improbable that q' is exactly the same as q, since we would expect the total amount of charge donated in the three-co-ordinate complex (q) to be slightly higher. The results of the previous papers [5,12] showing the tendency for ligands to donate less charge when other strong ligands are present suggest, however, that q will be less than $\frac{3}{2}q'$, the amount of charge donation expected on a purely additive model. If this inequality is substituted into equations (1) and (2), a decrease in isomer shift and quadrupole splitting is still predicted on going from $[AuL_2]^+$ to $[AuL_3]^+$.

TABLE 1

Mössbauer data[a] at liquid-helium temperature

	δ	Δ*E*	Γ	χ^2 [b]
	mm s^{-1}			
$[Au(PPh_3)_2][PF_6]$	5.06	9.43	2.67	413 (392) [c]
$[AuCl(PPh_3)_2]$	2.36	8.19	1.85	328 (241) [d]
$[AuI(PPh_3)_2]$	2.66	7.87	2.52	422 (390)
$[Au(PPh_3)_2(SCN)]$	2.46	8.52	2.69	403 (388)
$[Au(PEt_3)_2][PF_6]$	5.40	10.18	2.35	364 (390) [c]
$[AuCl(PEt_3)_2]$	4.25	8.93	2.19	418 (390)
$[AuI(PEt_3)_2]$	4.38	8.79	2.25	430 (390)
$[Au(C_5H_5N)(PPh_3)][PF_6]$	4.55	8.50	2.79	458 (390) [c]
$[Au(bipy)(PPh_3)][PF_6]$	2.81	6.76	3.7	383 (388) [e]
$[Au(phen)(PPh_3)][PF_6]$	2.82	7.05	2.24	394 (390)
$[Au(bipy)(PEt_3)][PF_6]$	2.96	7.33	2.34	633 (390) [f]
$[Au(PMe_2Ph)_2][PF_6]$	5.48	10.15	2.28	434 (388) [c]
$[Au(PMe_2Ph)_2(SnCl_3)]$	4.18	8.39	2.17	431 (390)
$[Au(pip)_2][PF_6]$	4.04	7.88	2.49	422 (389) [c]
$[AuCl(pip)_2]$	4.10	7.87	2.29	387 (389)
$[Au(etu)_2][PF_6]$	2.77	7.49	2.27	400 (390) [c]
$[AuCl(etu)_2]\cdot H_2O$	2.74	7.22	2.19	378 (390)
$[Au(PPh_3)(PPh_3S)][PF_6]$	4.25	8.02	2.32	400 (390) [c]
$[Au(PPh_3)\{Et_2P(S)(S)PEt_2\}][PF_6]$	3.77	7.59	2.45	394 (389)
$[Au(PPh_3)(PPh_3O)][PF_6]$	3.80	6.49	2.46	425 (389) [c]
$[Au(PPh_3)\{Ph_2P(O)CH_2CH_2(O)PPh_2\}][PF_6]$	3.92	6.71	2.12	366 (388)
$[Au(PPh_3)_3(SnCl_3)]$	1.64	3.57	1.99	177 (241) [d]

[a] Isomer shifts with respect to gold metal. Errors ±0.1 mm s^{-1} unless otherwise stated. [b] The number of degrees of freedom is given in parentheses. [c] From ref. 5. [d] Measured at P.C.M.U., Harwell. [e] Error ±0.2 mm s^{-1}. [f] Bad fit due to an instrumental error affecting the baseline; the absorption peaks were well fitted.

In most of the complexes we have studied the third ligand is generally rather weaker (*i.e.* more electronegative) than the other two. Thus, on going from $[AuL_2]^+$ to $[AuL_2X]$ we would not expect q to be much greater than q'. The symmetry is no longer D_{3d} and the asymmetry parameter η is no longer zero. Since the quadrupole splitting ΔE is given by (5) a value of η close to 1 may give a rather larger quadrupole splitting than expected from considering V_{zz} alone.

If X is a weak ligand, the Mössbauer parameters of $[AuL_2X]$ would be difficult to distinguish from those of a bent $[AuL_2]^+$ molecule, where the bending also has the effect

$$\Delta E = \tfrac{1}{2}eQV_{zz}\left(1 + \frac{\eta^2}{3}\right)^{\frac{1}{2}} \quad (5)$$

of increasing $6p$-orbital occupation and decreasing $6s$ occupation. However, all the two-co-ordinate gold compounds whose crystal structures have been published show linear or very nearly linear geometry.[5]

RESULTS

The Mössbauer data are given in Table 1.

$Au(PPh_3)_2X$ (X = PF_6, Cl, I, *or* SCN).—If we assume that the PF_6 complex is a two-co-ordinate salt {as is known for $[Au(PMePh_2)_2][PF_6]$ [13]}, then a sharp decrease in isomer shift, and a lesser decrease in quadrupole splitting, is noted for the other three ligands. The chloride is known to be three-co-ordinate,[1] and the similarity of the Mössbauer parameters of the iodide and thiocyanate suggest very strongly that they are also three-co-ordinate.

$[Au(PPh_3)L][PF_6]$ (L = C_5H_5N, *bipy, or phen*) *and* $[Au(bipy)(PEt_3)][PF_6]$.—The bipy complex is known to be three-co-ordinate [2] and shows a very substantial decrease in isomer shift and quadrupole splitting from the simple pyridine complex which we assume to be linear. This again confirms the general model discussed above. The similarity of the spectrum of the phen complex to that of bipy suggests that it is also three-co-ordinate. The ion $[Au(bipy)(PEt_3)]^+$ has similar δ and Δ*E* values to its triphenylphosphine analogue suggesting it to be three-co-ordinate.

$Au(PMe_2Ph)_2X$ (X = PF_6 *or* $SnCl_3$).—The decrease in Δ*E* and δ suggests the $SnCl_3$ complex to be three-co-ordinate,

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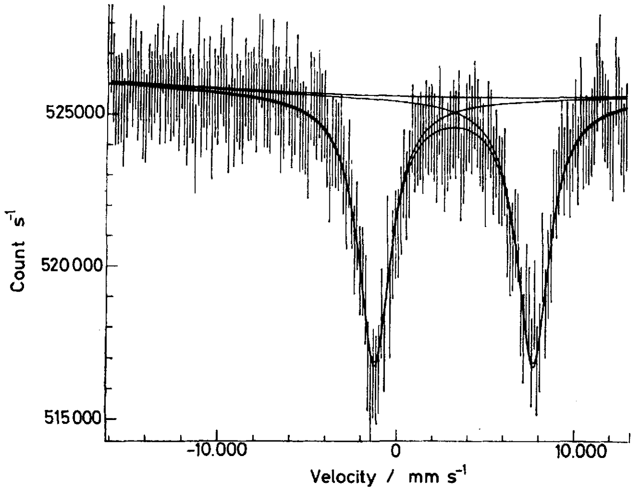
but the ^{119}Sn Mössbauer isomer shift corresponds more closely to a $[SnCl_3]^-$ anion.[14] This apparent paradox could be explained if the $[Au(PMe_2Ph)_2]^+$ species is significantly non-linear.

$Au(PEt_3)_2X$ (X = PF_6, Cl, *or* I).—The halides show a slight decrease in δ and ΔE by comparison with the PF_6 salt; however, the decrease is much less than for the two cases where three-co-ordination is established and is even less than for the ambiguous case of $Au(PMe_2Ph)_2(SnCl_3)$. In the preceding paper it was shown that lattice effects (due to ions not bonded to the gold complex) do not affect the gold Mössbauer parameters significantly, and this is confirmed by the two-co-ordinate species discussed below; the changes in δ and ΔE cannot be ascribed to lattice effects, and consequently it seems plausible to suggest an interaction with the third ligand, and an appreciable deviation from linearity.



Gold-197 Mössbauer absorption spectrum of $[AuCl(PEt_3)_2]$

AuL_2X [L = *piperidine* (*pip*) *or ethylenethiourea* (*etu*), X = Cl *or* PF_6].—Both these pairs of complexes have almost identical Mössbauer parameters for the $[PF_6]^-$ salt, and the possibly three-co-ordinate chloride complex, implying that all four have linear geometry with unco-ordinated anions. This is confirmed by an *X*-ray structure determination of $[AuCl(etu)_2]\cdot H_2O$,[15] which shows basically linear co-ordination but with an appreciable distortion (S–Au–S 167°). This distortion appears to be sufficient to reduce the quadrupole splitting slightly, but not enough to affect the isomer shift.

$[Au(PPh_3)(PPh_3S)][PF_6]$ *and* $[Au(PPh_3)\{Et_2P(S)(S)PEt_2\}][PF_6]$.—The decrease in δ and ΔE for the potentially bidentate sulphur ligand $Et_2P(S)(S)PEt_2$ is very small, and suggests that any interaction with the second sulphur group must be very weak. The 1,2-dithiodi-λ^5-phosphane can act as a simple non-chelating ligand (as in $[CuCl_2\{Me_2P(S)(S)PMe_2\}]$ [16]). The slight difference in the ligating powers of the two phosphines must also be considered. A crystal-structure determination of $[Au(PPh_3)\{Et_2P(S)(S)PEt_2\}][PF_6]$ is in progress.

$[Au(PPh_3)(PPh_3O)][PF_6]$ *and* $[Au(PPh_3)\{Ph_2P(O)CH_2CH_2(O)PPh_2\}][PF_6]$.—The general preparation mentioned above gave a somewhat unstable white powder with L = 1,2-bis(diphenylphosphoryl)ethane. This did not give entirely satisfactory analyses for $[Au(PPh_3)L][PF_6]$. Its Mössbauer parameters were, however, so close to those of the triphenylphosphine oxide complex that we assume that $[Au(PPh_3)L][PF_6]$ was the major constituent of the product and that it is a linear species with only one oxygen atom co-ordinated to the gold.[17]

$[Au(PPh_3)_3(SnCl_3)]$.—This complex, which Dilts and Johnson [18] characterised as tetrahedral, gives Mössbauer parameters which support the arguments presented above and its assigned structure. The low isomer shift implies a heavy 6*p* contribution to its bonding (and a relative depletion of the 6*s*) while the small quadrupole splitting is to be expected from a tetrahedral A_3BM species (M = a d^{10} ion, A and B are different ligands).

DISCUSSION

Table 2 shows the decrease in δ and ΔE on introduction of a new ligand L. For the established three-co-ordinate species there is always a large decrease in isomer shift, and this seems to be a good diagnostic test for three-co-ordination. The quadrupole splitting is much less sensitive to changes in co-ordination number, although in accordance with the model the decrease is always less than 33%. This different sensitivity could arise from three effects: (*a*) a strong '*p*-shielding' effect reducing $|\psi(0)|_{6s}^2$ (and consequently δ) on increasing occupation of the 6*p* orbitals; (*b*) a boosting of ΔE by the now non-zero (and possibly large) asymmetry parameter; and (*c*) a tendency for the ligands to bind more strongly with the 6*p* orbitals as the co-ordination number increases. We discount the first two effects as (*a*) would require a much larger effect than that found in ^{129}I Mössbauer spectroscopy [19] or predicted by theory (see previous paper), and (*b*) although probably detectable is somewhat self-compensating: in the complex $[AuL_2X]$ η will only be large if X is a very weak ligand, which will in turn reduce V_{zz}, so the total increase in quadrupole splitting will not be very great. The maximum effect of non-zero η is 15%.

The *X*-ray crystal structure of $[AuCl(PPh_3)_2]$ shows that the mean gold–phosphorus bond is appreciably

TABLE 2

The change in Mössbauer parameters (mm s^{-1}) in the presence of a third, possibly co-ordinated, ligand

Ion	New ligand	Change in isomer shift	Change in quadrupole splitting
$[Au(PPh_3)_2]^+$	Cl^-	−2.70	−1.24 [a]
	I^-	−2.40	−1.56
	$[SCN]^-$	−2.60	−0.91
$[Au(PMe_2Ph)_2]^+$	$[SnCl_3]^-$	−1.30	−1.76
$[Au(PEt_3)_2]^+$	Cl^-	−1.15	−1.25
	I^-	−1.02	−1.39
$[Au(C_5H_5N)(PPh_3)]^+$	C_5H_4N	−1.74	−1.74 [a]
$[Au(pip)_2]^+$	Cl^-	+0.06	−0.1
$[Au(etu)_2]^+$	Cl^-	−0.03	−0.27 [b]

[a] Known to be three-co-ordinate. [b] Known to be two-co-ordinate.

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longer (0.09 Å) than in [AuCl(PPh$_3$)] and slightly longer (0.015 Å) than [Au(PMePh$_2$)$_2$][PF$_6$].[13] We take this to indicate the expected weakening of the Au–P bond indicated by the n.q.r. results for [AuClL] [12] and mentioned above. We also suggest that the large decrease in isomer shift and relatively small decrease in quadrupole splitting may result from an increased 6*p* character in the Au–P bond as the internuclear distance increases, which would at once decrease δ and increase Δ*E*, as observed.

The variability of the hybridisation of the gold atom in its complexes was discussed in the previous paper, and we note that the same trends may be seen in the *X*-ray data for [AuCl(PPh$_3$)$_2$]: the P–Au–P bond angle is not 120° as expected for pure sp^2 hybrid orbitals, but 132° which could be explained by assuming more '*sp*' character to the Au–P bonds and more 'pure *p*' character to the Au–Cl bond, in agreement with Bent's rule.[20] However, much more crystallographic data are needed before any firm conclusions may be drawn. The large P–Au–P angle was attributed to steric interactions between the phosphines. Structural studies of a number of tetrahedral bis(phosphine)copper(I) [21] compounds have shown that as the P–Cu–P angle opens (implying more *s* character) the bond length shortens. This is in agreement with our results.

Our hybridisation model appears to explain the variation of the Mössbauer parameters quite successfully. A point-charge type of calculation is less successful as it fails to explain the large isomer-shift variation. Using our model, it seems likely that the two complexes discussed in the previous paper {[AuI(PPh$_3$)] and [Au(PPh$_3$)(SCN)]} which gave very low isomer-shift values may have either non-linear geometry or some form of molecular association (such as bridging ligands).

Bancroft pointed out that an additive-model treatment, using the p.q.s. values derived from complexes of the form [AuL$_2$]$^+$, predicts the quadrupole splitting of [AuCl(PPh$_3$)$_2$] very satisfactorily (Calc.: 8.29. Found: 8.19 mm s^{-1}) if the p.q.s. values are increased by 33% on going from *sp* to sp^2 hybridisation of the gold. The agreement is indeed remarkable, and a similar result is found for [AuCl(PEt$_3$)$_2$] (Calc.: 8.84. Found: 8.93 mm s^{-1}), but for the bipy complexes the agreement is much less satisfactory {[Au(bipy)(PPh$_3$)]$^+$, Calc.: 8.02. Found: 6.76. [Au(bipy)(PEt$_3$)], Calc.: 8.28. Found: 7.33 mm s^{-1}}. It is possible to ascribe these discrepancies to the distortion of the bipy complexes,[2] but it is equally possible that the success of the chlorobis(phosphine)gold calculations is coincidental. We note that n.q.r. results for In^{III}, a similar d^{10} system, show that the quadrupole coupling constant of InMe$_3$ is *ca.* 13% smaller than for [InMe$_2$]$^+$, contrary to the predictions of a purely additive model,[22] but in accord with the scheme allowing for varying ligand strength that we have proposed in this paper.

It is not yet clear what factors determine the co-ordination number of gold. Triethyl- and triphenyl-phosphine appear to be quite similar ligands as far as gold is concerned, and both give three-co-ordinate complexes with bipy, yet the behaviour of the halides is quite different. Similarly, a recent crystal-structure determination of [Au{P(C$_6$H$_{11}$)$_3$}$_2$(SCN)] [23] shows it to be two-ordinate with free [SCN]$^-$ ions in contrast to [Au(PPh$_3$)$_2$(SCN)] which we assigned as three-co-ordinate. Since there seems to be no obvious electronic effect we incline to believing crystal packing to be the dominant effect; this seems reasonable if the third ligand is only weakly bound [implying that gold(I) compounds are weak Lewis acids]. Since the Mössbauer evidence indicates the decrease of the 6*s* population at the expense of the 6*p*, this suggests that there is no massive change in the total amount of charge donated to the gold.

We have not considered π bonding in our discussion of the electronic environment of the gold atom in these complexes since the Mössbauer spectra discussed in the previous paper [5] suggested π bonding to be unimportant. As the gold–ligand bond lengths are generally greater for three- than for the equivalent two-co-ordinate species, it seems improbable that π acceptance is important.

Conclusions.—The variation of Mössbauer parameters with changing co-ordination of a gold(I) atom can be fairly easily explained using a simple model of the electronic distribution, and in many cases this permits an assignment of structure to complexes whose stereochemistry is in doubt. The method is not universally applicable, however, as many compounds fall in between sets of parameters for two- and three-co-ordination, possibly as a result of intermolecular association which is often encountered in gold chemistry. Further Mössbauer studies, in conjunction with *X*-ray crystal-structure determinations, should resolve some of these problems, and also throw further light on the hybridisation in such complexes.

[6/1926 *Received*, 14*th October*, 1976]

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