Studies in Mössbauer Spectroscopy. Part 9.[1] Gold-197 Spectra of Gold(I) Compounds †

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Gold-197 Mössbauer parameters are reported for gold(I) compounds of the type [AuClL] and $[AuL_2]^+$ (L = tertiary phosphine or arsine), which conform to the previously noted correlations of quadrupole splitting with isomer shift. The parameters clearly distinguish two-co-ordinate [AuClL] from $[AuL_2]^+$ and from three-co-ordinate $[AuClL_2]$. Scales of partial isomer shifts and quadrupole splittings are derived, but are of limited use.

LITTLE systematic study has been made of the Mössbauer spectra of gold(I) compounds. The d^{10} configuration and simple linear co-ordination frequently found make it a very favourable case for examining the effects which variations in the ligands have on the Mössbauer parameters, since there are no complications from non-bonding electrons, geometrical isomerism, *etc.* While data for several isolated compounds have been repored,[2-7] there has been only one major investigation, in which data for several compounds of the type [AuXL] were reported (L = neutral ligand, X = anionic ligand).[8] We have extended the range of compounds of this type (X = Cl) to include both uni- and bi-dentate ligands, and also report data for cationic complexes of the type $[AuL_2]Y$ (Y = ClO_4 or Cl). The applicability of the additivity model to Au^I is also examined.

RESULTS AND DISCUSSION

Mössbauer Data.—The data are given in Table 1 together with other values for gold(I) compounds. For $[AuCl(PPh_3)]$ and $[Au(AsPh_3)Cl]$ the quadrupole splittings (q.s.) agree well with previous reports,[2,8] but our isomer shifts (i.s.) are a little lower than those found by Charlton and Nicholls;[8] this presumably represents slight differences in the sources used. The i.s. value for $[Au(AsPh_3)Cl]$ given by Wagner and his co-workers [2] is much higher than the other two values and is presumably in error.

The new data conform to the strong positive correlation of q.s. with i.s. noted by other workers [3,4,8] (Figure 1). Since the i.s. represents the effect of donation into the 6*s* orbital of the gold atom and the q.s. that into the 6*p* orbital, such a correlation is to be expected, although it would not necessarily be linear, and a slight positive curvature is seen. The compounds containing the softest ligands (phosphines, cyanide ion, and σ-bonded carbanions) gave the highest values of both parameters, demonstrating that these ligands are effective donors to Au^I. For compounds [AuClL] the donor power thus increases in the order of donor atoms S < As < P and this is consistent with the report that the ligand *o*-MeS·C_6H_4·$AsMe_2$ bonds to Au^I *via* the arsenic rather than the sulphur atom.[9] The π-bonded olefins and acetylenes are relatively poor donors.

Unidentate ligands. The bis(phosphine) compounds gave parameters distinctly different from those of the corresponding [AuClL], demonstrating that the additional ligand is bonded directly to the gold atom. In the majority of cases, both the i.s. and the q.s. were significantly greater than for the monophosphine complexes, but fit the q.s.–i.s. correlation, consistent with their being linear two-co-ordinate compounds of the type $[AuL_2]Y$. Other physical data and the method of preparation are also consistent with this formulation.[10] The compound $AuCl(PMe_2Ph)_2$ has similar parameters and is presumably also ionic, $[Au(PMe_2Ph)_2]Cl$. However, the parameters for $[AuCl(PPh_3)_2]$ which are considerably lower than those of $[Au(PPh_3)_2][ClO_4]$, and very different from those of $[AuCl(PPh_3)]$, do not fit the q.s.–i.s. correlation. This difference is consistent with the recent report that, in the benzene solvate of this compound, the gold atom is trigonally three-co-ordinate.[11]

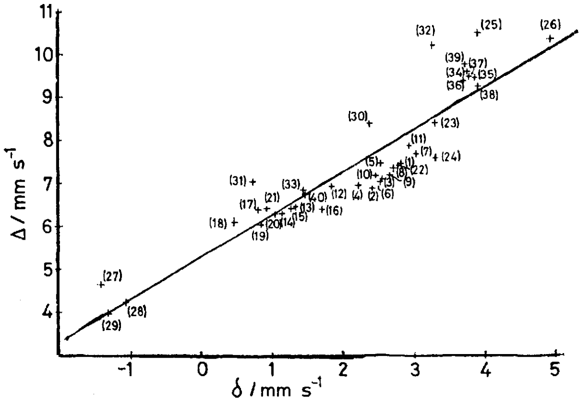

FIGURE 1 Plot of quadrupole splitting against isomer shift for two-co-ordinate gold(I) compounds. The numbering of the points corresponds to Table 1. The least-squares line is: $\Delta/\mathrm{mm\ s^{-1}} = (0.987 \pm 0.066)\ \delta/\mathrm{mm\ s^{-1}} + (5.30 \pm 0.18)$; r^2 0.849

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† No reprints available.

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It is generally found that the i.s. decreases (for positive $\delta R/R$) with increasing co-ordination number, owing to the combined effects of bond lengthening and increased shielding through the increase in *p* character of the metal–ligand bonds. The relatively large decrease in i.s. is consistent with the large range of values found for gold(I) compounds (−1.3 to 4.9 mm s^{-1}), *i.e.* this parameter is a very sensitive indicator of electron density. The q.s. is intermediate between those of $[AuCl(PPh_3)]$ and $[Au(PPh_3)_2]^+$.

The i.s. and q.s. values reported by Charlton and Nicholls [8] for $[AuI(PPh_3)]$ are very similar to those found here for $[AuCl(PPh_3)_2]$, suggesting that these authors may actually have measured $[AuI(PPh_3)_2]$, which would presumably also be three-co-ordinate.

Bidentate ligands. For the potentially bidentate ligands, the Mössbauer data confirm the results of other physical measurements,[10] that the compounds should be formulated with each donor atom bonding to a separate AuCl unit $[ClAu(L{-}L)AuCl]$, rather than as di- or polymeric ionic compounds, $[Au(L{-}L)][AuCl_2]$ or $[\{-LAu(L{-}L)AuL-\}_n]Cl_{2n}$. Although the thiocyanato-derivative $[Au(\textit{cis}\text{-}Ph_2PCH{:}CHPPh_2)(SCN)]$ appears to be a chelate with three-co-ordinate gold,[10] the Mössbauer parameters for the 1 : 2 complex with AuCl show that it should be formulated in a similar way to the other compounds, as *cis*-$[ClAu(Ph_2PCH{:}CHPPh_2)AuCl]$. The i.s. and q.s. for this compound are appreciably smaller than those for the complex of the *trans* ligand. It is unlikely that a change in geometric configuration would produce this effect. However, the *cis* ligand is co-ordinated to two gold atoms while the *trans* ligand carries only one; the latter may therefore be able to act as a significantly better donor. There is a similar difference between the 1 : 2 complex of *cis*-$Me_2AsCH{:}CHAsMe_2$ and the 1 : 1 complex of $AsPh_3$.

TABLE 1

Gold-197 Mössbauer data (4.2 K) [a]

Compound	δ [b] mm s^{-1}	Δ mm s^{-1}	Γ_1 mm s^{-1}	Γ_2 mm s^{-1}	χ^2 [c]	Ref.	Key to Figure 1
$[AuCl(PPh_3)]$	2.82(2)	7.45(4)	2.32(6)	2.18(6)	0.86	*d*	(1)
	2.96(7)	7.47(13)				8	
	2.83(3)	7.34(7)				2	
$[AuCl(PMePh_2)]$	2.40(2)	6.89(4)	2.19(7)	1.93(6)	1.00	*d*	(2)
$[AuCl(PEtPh_2)]$	2.54(1)	7.09(2)	2.08(4)	2.11(4)	1.22	*d*	(3)
cis-$[ClAu(Ph_2PCH{:}CHPPh_2)AuCl]$	2.21(2)	6.94(4)	1.93(6)	2.03(6)	0.78	*d*	(4)
$[AuCl(\textit{trans}\text{-}Ph_2PCH{:}CHPPh_2)]$	2.52(4)	7.46(8)	2.04(11)	2.15(12)	0.83	*d*	(5)
$[ClAu(Ph_2PCH_2PPh_2)AuCl]$ [e]	2.52(14)	7.03(27)	1.97(18) [f]		0.98	*d*	(6)
$[ClAu(Ph_2P[CH_2]_6PPh_2)AuCl]$	3.03(3)	7.68(6)	2.06(8)	1.96(8)	1.14	*d*	(7)
$[ClAu(Ph_2P[CH_2]_{12}PPh_2)AuCl]$	2.70(2)	7.36(4)	1.92(6)	2.03(6)	0.91	*d*	(8)
$[AuCl(PMe_2Ph)]$	2.65(4)	7.18(7)	2.28(10)	2.29(11)	1.28	*d*	(9)
$[AuCl\{P(C_6H_4Me\text{-}p)_3\}]$	2.45(3)	7.16(5)	2.57(8)	2.27(8)	1.29	*d*	(10)
$[AuCl\{PPh_2(C_6F_5)\}]$	2.93(3)	7.87(4)				8	(11)
$[Au(AsPh_3)Cl]$	1.83(1)	6.92(2)	2.22(3)	2.06(3)	1.06	*d*	(12)
	1.92(3)	7.00(7)				8	
	2.76(6)	7.40(10)				2	
cis-$[ClAu(Me_2AsCH{:}CHAsMe_2)AuCl]$	1.32(2)	6.45(4)	2.26(6)	2.52(7)	1.02	*d*	(13)
$[ClAu(MeS[CH_2]_2SMe)AuCl]$	1.13(6)	6.30(11)	2.35(16)	2.10(18)	0.59	*d*	(14)
$[AuCl(SMe_2)]$	1.26(2)	6.42(3)				8	(15)
$[AuCl(NC_5H_5)]$	1.7(1)	6.4(2)				8	(16)
$[Au(MeC{\vdots}CMe)Cl]$	0.79(2)	6.38(4)				5	(17)
$[Au(cot)Cl]$ [g]	0.45(8)	6.10(16)				6	(18)
$[Au(C_{10}H_{12})Cl]$	0.83	6.04				4	(19)
$[Au(C_{16}H_{32})Cl]$	1.03	6.29				4	(20)
$[Au(C_{18}H_{36})Cl]$	0.91	6.41				4	(21)
$[AuBr(PPh_3)]$	2.76(6)	7.40(10)				8	(22)
$[AuI(PPh_3)]$	1.24(6)	8.3(1)				8	
$[Au(N_3)(PPh_3)]$	3.3(2)	8.4(2)				8	(23)
$[Au(O_2CMe)(PPh_3)]$	3.3(2)	7.6(2)				8	(24)
$[Au(CN)(PPh_3)]$	3.9(2)	10.5(2)				8	(25)
$[AuMe(PPh_3)]$	4.93(4)	10.35(6)				8	(26)
AuCl	−1.42(1)	4.65(1)				3	(27)
AuBr	−1.07(1)	4.23(4)				3	(28)
AuI	−1.32(3)	3.98(1)				3	(29)
$Au[CN]$	2.37(2)	8.39(2)				8	(30)
$Na_3[Au(S_2O_3)_2]$	0.72(29)	7.04(4)				3	(31)
$K[Au(CN)_2]$	3.25(8)	10.21(6)				3	(32)
$[AsPh_4][Au(N_3)_2]$	1.43	6.84				4	(33)
$Et_2P[CH_2AuCH_2]_2PEt_2$	3.76(4)	9.60(10)				2	(34)
$[Au(PPh_3)_2][ClO_4]$	3.87(5)	9.46(9)	2.18(12)	2.58(15)	0.92	*d*	(35)
$[Au(PMePh_2)_2][ClO_4]$	3.71(2)	9.38(4)	2.01(6)	1.98(6)	0.93	*d*	(36)
$[Au(PEtPh_2)_2][ClO_4]$	3.78(3)	9.49(6)	2.10(9)	1.89(9)	0.90	*d*	(37)
$[Au(PMe_2Ph)_2]Cl$	3.91(7)	9.26(14)	2.20(20)	2.11(20)	0.66	*d*	(38)
$[Au(PEt_2Ph)_2][ClO_4]$	3.72(4)	9.77(7)	2.04(8)	2.38(12)	1.00	*d*	(39)
$[AuCl(PPh_3)_2]$	1.12(3)	8.25(5)	1.98(7)	2.22(8)	0.98	*d*	
$[Au(MeC{\vdots}CMe)_2][AuCl_4]$ [h]	1.46(3)	6.74(3)				5	(40)

[a] Fitting errors are given in parentheses. Reproducibility is *ca.* ±0.03 mm s^{-1}. [b] Relative to ^{197}Pt source at 4.2 K. [c] Per degree of freedom, usually 240—241. [d] This work. [e] Major component. [f] Widths constrained to be equal. [g] cot = Cyclo-octatetraene. [h] Values for cation only.

The spectrum of $[Au_2Cl_2(Ph_2PCH_2PPh_2)]$ showed two doublets which could only be satisfactorily resolved by constraining the linewidths. The major species (*ca.* 65%) gave parameters similar to those of the other bidentate digold compounds. The parameters of the minor species [δ 3.34(13) mm s^{-1}, Δ 8.96(26) mm s^{-1}] suggest that it contains a cationic species with two phosphorus atoms co-ordinated to the gold atom. Since the sample was analytically pure, the counter ion would be expected to be $[AuCl_2]^-$, but no sign of a third component could be seen in the spectrum, and the linewidths did not justify a search for further peaks under the absorption envelope. It is possible that some rearrangement or decomposition occurred when the sample was mulled in hot paraffin wax (the supporting agent), since a similar effect was found with one sample of $[AuCl(PPh_3)_2]$, which gave a spectrum corresponding to that of $[AuCl(PPh_3)]$.

Additivity model. The regular increases in both q.s. and i.s. with increasing ligand softness suggest that attempts to parameterise these quantities might be successful. Good scales of partial quadrupole splittings (p.q.s.s) have been constructed for low-spin Fe^{II},[12] Sn^{IV},[13] and Sb^{V}.[14] A partial-isomer-shift scale (or partial centre shift, p.c.s.) can also be constructed for the first of these but not for tin or antimony. Data for Ir^{III} have recently been analysed to give p.c.s. and p.q.s. scales with moderate success.[15]

Preliminary examinations of the data were not encouraging. For instance, the range of i.s. values is larger for [AuClL] (L = unidentate tertiary phosphine) than for the corresponding $[AuL_2]^+$ species, and the ligands do not give the same order of increasing i.s. in both series. The additivity treatment suggests that the ranges should be the same. Similar discrepancies were found in the q.s. data for these two series: the ranges of q.s. values are similar, while the additivity model anticipates a ratio greater than 1 : 1. However, the i.s. and q.s. ranges are quite small and the discrepancies could be due to experimental errors. An alternative test would be to compare the data for [AuXL] with the average of those for $[AuL_2]^+$ and $[AuX_2]^-$; this would give values of 3.56 and 9.83 mm s^{-1} respectively for the i.s. and q.s. of $[Au(CN)(PPh_3)]$ and of 2.65 and 8.15 mm s^{-1} for $[Au(N_3)(PPh_3)]$. All these values are smaller than those observed, especially for the azido-complex.

Nevertheless, it was felt desirable to analyse the data more fully, in order to obtain a statistical measure of the errors of the treatment and to compare the results with those obtained for Ir^{II}. Correlations between different systems may be expected when the parameters have been derived from isoelectronic and isostructural series of compounds of elements close together in the Periodic Table, and q.s. data for Sn^{IV} and Sb^{V} have been shown to be linearly related.[16] It has also been demonstrated that a change in hybridisation affects only the scale of values but not the relative positions of different ligands, *e.g.* for Sn^{IV}, p.q.s. values for six-co-ordination parallel those for four-co-ordination.[17] It seems reasonable, therefore, to attempt a correlation between the parameters for Au^{I} and Ir^{III}. Although they are neither isostructural nor isoelectronic, both have closed-shell configurations (d^{10} and t_{2g}^{6}) and may be expected to form bonds of similar degrees of covalency, *etc.*

TABLE 2

Derivation of p.c.s.(Cl^-) and p.c.s.(L)

L	δ(AuClL) mm s^{-1}	$\frac{1}{2}\delta(AuL_2^+)$ mm s^{-1}	p.c.s.(Cl^-) mm s^{-1}	p.c.s.(L) mm s^{-1}	$\frac{1}{2}\delta(AuL_2^+)$ − p.c.s.(L) mm s^{-1}
PPh_3	2.82	1.94	0.88	2.13	−0.19
$PMePh_2$	2.40	1.86	0.54	1.71	+0.15
$PEtPh_2$	2.54	1.89	0.65	1.85	+0.04
PMe_2Ph	2.65	1.95	0.70	1.96	−0.01
			Average 0.69 ± 0.23		

It is usually necessary to adopt an arbitrary standard for p.c.s. and p.q.s. scales, the normal choice being to set the values for Cl^- equal to zero. In the case of Au^{I}, however, absolute values can be obtained. In four cases data are available for the pairs of compounds $[AuL_2]^+$ and [AuClL], giving four independent estimates of p.c.s.(Cl^-) and p.q.s.(Cl^-).

Partial isomer shifts. Relations (1)—(3) apply. The

$$\delta(AuL_2^+) = 2 \text{ p.c.s. (L)} \qquad (1)$$

$$\delta(AuClL) = \text{p.c.s.(L)} + \text{p.c.s.}(Cl^-) \qquad (2)$$

$$\text{p.c.s.}(Cl^-) = \delta(AuClL) - \tfrac{1}{2}\delta(AuL_2^+) \qquad (3)$$

four sets of data (Table 2) give an average value for p.c.s.(Cl^-) of 0.60 ± 0.23 mm s^{-1} (the error given is the standard error of the mean, $\pm ts/n^{\frac{1}{2}}$). This value may then be reapplied to the original data to obtain values for p.c.s.(L) which may be compared with those obtained from p.c.s.(L) = $\frac{1}{2}\delta(AuL_2^+)$ (Table 2). In two cases the agreement is rather poor. These values can also be used to derive p.c.s. values for other ligands, using the i.s. data for [AuXL] (Table 3). In two cases the values thus obtained can be compared with $\frac{1}{2}\delta(AuX_2^-)$: for X = CN agreement is moderately good, but for X = N_3 the two values are very different. For five ligands comparison can be made with the corresponding values derived from iridium(III) data.[15] Although the points

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are rather scattered [Figure 2(*a*)], there was a reasonable positive correlation (r^2 0.65).

Partial quadrupole splittings. The sign of the electric-field gradient in gold(I) compounds is usually assumed to be negative,[3] by virtue of the fact that the valence shell of the gold atom is receiving negative charge density donated by the ligands and there is no contribution from the closed-shell configuration of the gold(I) atom itself. Since the quadrupole moment of ^{197}Au is positive, the quadrupole coupling constants must be negative, and the p.q.s. values are expected to be negative also. On scales in which p.q.s.(Cl^-) is taken to be zero, values for most other ligands are negative and become more negative as the ligands become better donors.

TABLE 3

Partial-isomer-shift values (mm s^{-1})

L	p.c.s.(L)	p.c.s.$(L)_{Ir}$ [a]	Key to Figure 3
$MeS[CH_2]_2SMe$	0.42		(1)
SMe_2	0.57	0.30	(2)
cis-$Me_2AsCH{:}CHAsMe_2$	0.63		(3)
Br^-	0.63		(4)
Cl^-	0.69	0.00	(5)
C_5H_5N	1.0	0.28	(6)
$AsPh_3$	1.14		(7)
$[N_3]^-$	1.2 [b]		(8)
$[O_2CMe]^-$	1.2		(9)
cis-$Ph_2PCH{:}CHPPh_2$	1.52		(10)
$PMePh_2$	1.71		(11)
$P(C_6H_4Me$-*p*$)_3$	1.76		(12)
$[CN]^-$	1.8 [c]	0.52	(13)
trans-$Ph_2PCH{:}CHPPh_2$	1.83		(14)
$PEtPh_2$	1.85		(15)
$Ph_2PCH_2PPh_2$	1.86		(16)
PMe_2Ph	1.96	0.48	(17)
$Ph_2P[CH_2]_{12}PPh_2$	2.01		(18)
PPh_3	2.13		(19)
$Ph_2P[CH_2]_6PPh_2$	2.34		(20)
$[CH_3]^-$	2.8		(21)

[a] Ref. 15. [b] $\frac{1}{2}\delta[Au(N_3)_2^-]$ 0.72 mm s^{-1}. [c] $\frac{1}{2}\delta[Au(CN)_2^-]$ 1.63 mm s^{-1}.

TABLE 4

Derivation of p.q.s.(Cl^-) and p.q.s.(L)

L	$\frac{1}{2}\Delta'(AuClL)$ mm s^{-1}	$\frac{1}{4}\Delta'(AuL_2^+)$ mm s^{-1}	p.q.s.(Cl^-) mm s^{-1}	p.q.s.(L) mm s^{-1}	$\frac{1}{4}\Delta'(AuL_2^+)$ − p.q.s.(L) mm s^{-1}
PPh_3	−3.73	−2.37	−1.36	−2.50	+0.13
$PMePh_2$	−3.45	−2.35	−1.10	−2.22	−0.13
$PEtPh_2$	−3.55	−2.38	−1.17	−2.32	−0.06
PMe_2Ph	−3.59	−2.32	−1.27	−2.37	+0.05
		Average	−1.22 ± 0.18		

Defining[16] $\Delta' = \frac{1}{2}e^2qQ$, we have expressions (4)—(6).

$$\Delta'(AuL_2^+) = 4\ \text{p.q.s.(L)} \quad (4)$$

$$\Delta'(AuClL) = 2\ \text{p.q.s.(L)} + 2\ \text{p.q.s.}(Cl^-) \quad (5)$$

$$\text{p.q.s.}(Cl^-) = \tfrac{1}{2}\Delta'(AuClL) - \tfrac{1}{4}\Delta'(AuL_2^+) \quad (6)$$

This treatment (Table 4) gave an average value for p.q.s.(Cl^-) of −1.22 ± 0.18 mm s^{-1}, which is rather better defined than the corresponding p.c.s. value. However, this value yields p.q.s.(L) values which are in only modest agreement with those derived from p.q.s.(L) = $\frac{1}{4}\Delta'(AuL_2^+)$ (remembering that these parameters must be doubled or quadrupled in calculating quadrupole splittings). Values for other ligands were derived (Table 5) and, in the two cases where independent checks can be made, agreement is good for $[N_3]^-$ and moderate for $[CN]^-$. In this case, correlation with the iridium(III) scale is rather better [Figure 2(*b*)], the four points giving r^2 0.89.

Since there is an approximately linear relation between i.s. and q.s., a similar correlation of p.c.s. with p.q.s. might be expected, as was indeed found (Figure 3), although the points were again rather scattered. The gradient was *ca.* −0.5 times that of Figure 1, as would be expected.

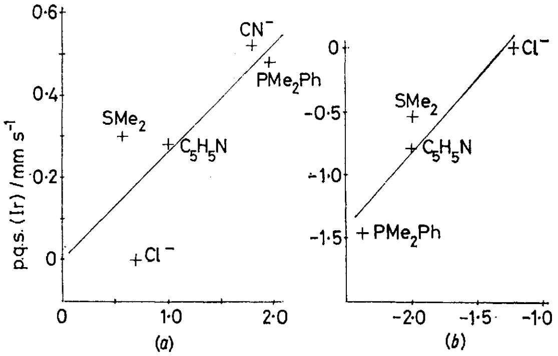

FIGURE 2 Correlation of (*a*) p.c.s. values and (*b*) p.q.s. values for Au^I with those for Ir^{III}

Conclusions.—Gold-197 Mössbauer data are of value in diagnosing the structural type of gold(I) compounds. Two-co-ordinate [AuXL] and $[AuL_2]^+$ and three-co-ordinate $[AuXL_2]$ compounds can all be clearly distinguished, and the parameters reflect the bonding characteristics of the ligands. In the above discussions no account has been taken of π bonding. Such back donation is unlikely for a d^{10} ion, but if it occurred it would

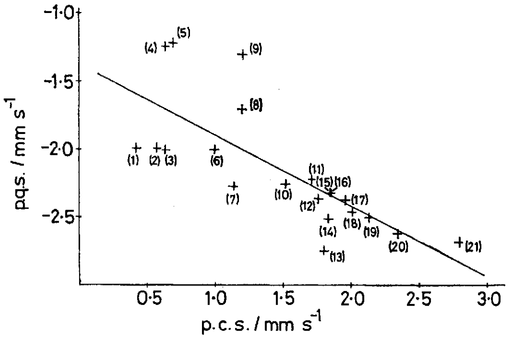

FIGURE 3 Correlation between p.q.s. and p.c.s. values. The numbering of the points corresponds to Table 3. The least-squares line is: p.q.s./mm s^{-1} = (−0.521 ± 0.104) p.c.s./mm s^{-1} − (1.37 ± 0.17); r^2 0.568

have the effect of relatively increasing the i.s. and decreasing the q.s. Since none of the data considered deviates markedly from the q.s.–i.s. correlation, even for olefin-, acetylene-, or cyano-complexes, it may be concluded that π-bonding effects are either negligible or *increase uni*formly along the series of compounds.

The additivity model is clearly not very satisfactory.

TABLE 5

Partial-quadrupole-splitting values (mm s^{-1})

L	p.q.s.(L)	p.q.s.$(L)_{Ir}$ [a]
Cl^-	−1.22	0.00
Br^-	−1.24	
$[O_2CMe]^-$	−1.3	
$[N_3]^-$	−1.7 [b]	
$MeS[CH_2]_2SMe$	−1.94	
SMe_2	−1.99	−0.54
C_5H_5N	−2.0	−0.79
cis-$Me_2AsCH{:}CHAsMe_2$	−2.00	
$PMePh_2$	−2.22	
cis-$Ph_2PCH{:}CHPPh_2$	−2.25	
$AsPh_3$	−2.27	
$PEtPh_2$	−2.32	
$Ph_2PCH_2PPh_2$	−2.32	
$P(C_6H_4Me\text{-}p)_3$	−2.36	
PMe_2Ph	−2.37	−1.46
$Ph_2P[CH_2]_{12}PPh_2$	−2.46	
PPh_3	−2.50	
trans-$Ph_2PCH{:}CHPPh_2$	−2.51	
$Ph_2P[CH_2]_6PPh_2$	−2.62	
$[CH_3]^-$	−2.68	
$[CN]^-$	−2.75 [c]	

[a] Ref. 15. [b] $\frac{1}{4}\Delta'[Au(N_3)_2{}^-]$ −1.71 mm s^{-1}. [c] $\frac{1}{4}\Delta'[Au(CN)^-{}_2]$ −2.55 mm s^{-1}.

With the data presently available the p.c.s. and p.q.s. values have associated errors of *ca.* 0.2 mm s^{-1}, so that calculated and observed parameters could disagree by 0.4—0.8 mm s^{-1}, which renders the treatment of very limited value. Its use within a class of closely related compounds (*e.g.* of phosphine complexes) would be less approximate, but more data are needed.

The breakdown of the additivity model is presumably due to the high degree of covalency of the gold–ligand bonds coupled with the high polarisability of the soft metal ion. It is noticeable that the model becomes less satisfactory as the polarisability of the central metal atom increases: good agreement with observation is achieved for iron and tin, but in the latter case discrepancies have been found [18] which suggest that p.q.s. values are not independent of the other ligands present, *i.e.* the electron distribution in one bond is dependent on the other bonds present *via* the *cis* and *trans* influences. A similar suggestion has recently been made to explain the failure of the additivity model for Ir^{III},[15] and the operation of both *cis* and *trans* influences in platinum(II) complexes has been clearly shown by ^{129}I Mössbauer spectroscopy.[19,20] These influences should become increasingly important as the bonding becomes more covalent and the metal atom more polarisable, and they are readily discernible in, for example, the i.r. spectra of [AuClL] [10]

EXPERIMENTAL

The compounds were prepared by variations of established methods and will be fully described elsewhere.[10] Gold-197 Mössbauer spectra were obtained by PCMU, Harwell, with both source and sample immersed in liquid helium (4.2 K), using a ^{197}Pt source (also the i.s. standard) with a sodium iodide scintillation counter. Typical absorption intensities for 300—500-mg samples were *ca.* 0.5%. Data were analysed by the usual least-squares method, fitting unconstrained Lorentzian peaks. For $[Au_2Cl_2(Ph_2PCH_2\cdot PPh_2)]$ the two peaks of each doublet were constrained to have equal widths.

We thank the S.R.C. for provision of a Research Studentship (to P. D. R.) and for an allocation of PCMU spectrometer time.

[6/1836 *Received*, 30*th September*, 1976]

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