Structure and Bonding in Gold(I) Compounds. Part 1. The *trans* Influence in Linear Complexes

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The *trans* influence in linear gold(I) complexes [AuClL] has been studied by ^{35}Cl n.q.r. spectroscopy [L = RNC (R = Ph, *p*-MeOC$_6$H$_4$, or C$_6$H$_{11}$), Cl$^-$, C$_5$H$_5$N, PR'$_3$ (R' = Et, Ph, C$_6$H$_{11}$, Cl, OMe, or OPh), AsPh$_3$, PPh$_3$S, or SMe$_2$]. The ^{35}Cl n.q.r. frequencies show a high senstitvity to the *trans* ligand, and may be related to the bonding properties of this ligand. It is concluded that σ-bonding effects are dominant. The results are significantly different from those obtained from similar studies of square-planar platinum(II) complexes.

THE *trans* influence, the effect on a given metal–ligand bond of the ligand *trans* to that M–L bond in the ground state, is a well established phenomenon which has recently been reviewed.[1] This paper presents the results of the study of a series of linear gold(I) complexes [AuClL], where the *trans* influence of L on the AuCl bond is assessed by measurement of the chlorine nuclear quadrupole resonance (n.q.r.) frequency. This approach has several advantages. (*i*) The n.q.r. frequency depends on the immediate environment of the chlorine nucleus; the

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[1] T. G. Appleton, H. C. Clark, and L. E. Manzer, *Co-ordination Chem. Rev.*, **1973**, **10**, 335.

measurement is thus 'localised' on the chlorine atom and any variation of frequency reflects a change in the AuCl bond character. (*ii*) The choice of simple linear complexes enables any *cis* influences (effects from ligands other than the *trans* ligand) to be ignored. Molecular-orbital (m.o.) calculations have suggested that the *cis* influence may be comparable in magnitude to the *trans*.[2] (*iii*) As ^{197}Au has a convenient Mössbauer resonance, it is possible to gain the same sort of information about the central atom as the n.q.r. frequency gives about the chlorine atom (see following paper); both techniques measure electron distribution.

All the compounds studied here were assumed to be linear and two-co-ordinate, although *X*-ray crystal-structure determinations are only available for two of the compounds studied. However, the ^{197}Au Mössbauer data suggest very strongly that all the compounds have the assigned co-ordination geometry.

EXPERIMENTAL

All the n.q.r. data were obtained using a Decca Radar NQR spectrometer. The signals were almost invariably weak, and consequently slow scan speeds and long time constants were used; the spectrometer was modified to give a 50-s time constant, and the scanning speeds used were of the order of 300 kHz h^{-1}. All the scans were made with increasing and decreasing frequency to confirm the signals, and the resonances were measured at different temperatures; the variation of the chlorine-35 resonance frequency with temperature showed a linear decrease, although two samples {[AuCl(PPh$_3$)] and [AuCl(py)] (py = pyridine)} showed one peak above 273 K and two below, presumably because of a phase change. The reproducibility and temperature variation of the signals discounts the possibility that the signals are spurious. Interestingly, several complexes (notably [AuCl(PPh$_3$)], [AuCl{P(C$_6$H$_{11}$)$_3$}], and [Au(AsPh$_3$)Cl]) gave much stronger signals after heating in sealed ampoules *ca.* 20 °C below the melting point. The slight colouration that this produced suggests that slight decomposition had occurred, and the strongest signal observed was from [AuCl(SMe$_2$)], which is light sensitive and also decomposes slightly. In contrast to normal experience, slowly grown, perfect, crystals gave weaker signals than the heated samples.

Chlorine-37 signals were searched for, but found only for [AuCl(SMe$_2$)]; however, scans above the observed frequencies showed no signal, confirming that the observed signals were due to ^{35}Cl and *not* ^{37}Cl. Zeeman modulation and maximum radiofrequency (r.f.) power were used. Samples were typically 1—2 g. In order to facilitate comparisons with Mössbauer data in the following paper, the reported frequencies were extrapolated to 0 K.

Preparations.—Most of the [AuClL] species were prepared by literature methods: L = P(C$_6$H$_{11}$)$_3$,[3] PPh$_3$,[4] AsPh$_3$,[5] PEt$_3$,[6] isocyanides,[7] SMe$_2$,[8] pyridine,[9] and P(OMe)$_3$.[10] The following complexes had already been described but were made by methods other than those in the literature.

[AuCl{P(OPh)$_3$}].[10] The complex [AuCl(SMe$_2$)] (1.0 g) was added to excess of triphenyl phosphite (4 cm^3) and warmed to 60 °C to effect solution. The solution was allowed to cool and transferred to a refrigerator for 3 h. The complex separated as colourless crystals, which were filtered off, washed with diethyl ether, and dried *in vacuo*, yield 1.3 g (70%) (Found: C, 39.8; H, 2.8. $C_{18}H_{15}AuClO_3P$ requires C, 39.8; H, 2.8%).

[AuCl(PPh$_3$S)].[11] The complex [AuCl(SMe$_2$)] (1.0 g) was dissolved in the minimum of dichloromethane and a concentrated solution of PPh$_3$S (1.0 g) in dichloromethane was added. The combined solution was concentrated to about three quarters of its original volume *in vacuo*, and diethyl ether was added until the solution became cloudy. The solution was placed in a refrigerator overnight, when the product separated as white crystals which were filtered off, washed with diethyl ether, and dried *in vacuo*, yield 1.32 g. Another crop was obtained from the filtrate, total yield 1.66 g (93%) (Found: C, 41.4; H, 3.0. $C_{18}H_{15}AuClPS$ requires C, 41.0; H, 2.9%).

[AuCl(PCl$_3$)].[12] Gold (1.66 g) was converted into tetrachloroauric(III) acid and thence to [Au(CO)Cl] in SOCl$_2$ suspension.[13] Excess of PCl$_3$ (4 cm^3) was added gradually to the suspension causing immediate effervescence and a voluminous crystalline white product. This was filtered off and dried *in vacuo*. Another crop was obtained by cooling the filtrate, total yield 2.24 g (71%) of cream, very moisture-sensitive, crystals. This complex showed the expected PCl$_3$ n.q.r. signals at 29.98, 29.58, and 29.36 MHz (77 K) {PCl$_3$, 26.21 and 26.10 MHz; [CuCl(PCl$_3$)], 27.98 MHz}.[14]

[AuCl$_2$]$^-$.[15] This ion has already been reported as its tetra-alkylammonium salts; these are sensitive to moist air. The tetraphenylarsonium salt is stable in air and can moreover be obtained in good yield as follows. The salt [AsPh$_4$]-[AuCl$_4$] (2.17 g) was partly dissolved in absolute ethanol (200 cm^3), and a solution of PhNHNH$_2$·HCl (0.22 g) in absolute ethanol (20 cm^3) was added. The solution was heated under reflux for 2.5 h, with a small excess of reductant (*ca.* 0.05 g) being added gradually over this period. The colour of the solution changed from orange to light pinkish brown. The solution was then decanted from the small amount of gold which had precipitated, and placed in a refrigerator overnight. The product separated as fine white crystals, which were filtered off, washed with diethyl ether, and dried *in vacuo*, yield 1.60 g (82%) (Found: C, 44.3; H, 3.4. $C_{24}H_{20}AsAuCl_2$ requires C, 44.3; H, 3.1%).

Interpretation of Results.—The electric field gradient (e.f.g.) at the chlorine nucleus (proportional for cylindrical symmetry to the measured n.q.r. frequency, ν_{Cl}) arises from asymmetry in the occupation of the valence shell of the chlorine atom.[16] We ignore the lattice effects arising from charge at some distance from the chlorine atom; most of

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[15] P. Braunstein and R. J. H. Clark, *J.C.S. Dalton*, 1973, 1845.

[16] See E. A. C. Lucken, 'Nuclear Quadrupole Coupling Constants,' Academic Press, London, 1969, ch. 7.

the complexes studied here are neutral, and furthermore the ^{197}Au Mössbauer spectra of charged complexes discussed in the following papers show no observable lattice effects. We also assume that the chlorine $3s$ orbital plays no part in bonding; in view of the high ionic character of the chlorine ligand this is almost certainly justified. The e.f.g. may thus be considered to arise exclusively from imbalance in the $3p$ shell of the chlorine atom, which, in turn, will be determined by (*a*) σ donation from the AuL moiety into the chlorine $3p_z$ orbital (the z axis lying along the LAuCl axis), and (*b*) π acceptance by AuL from the chlorine $3p_x$ and $3p_y$ orbitals.

If the occupation of the $3p_i$ orbital is denoted by n_i then the Townes–Dailey relation [16,17] gives (1) assuming that the

$$|\nu_{\text{Cl}}| = 27.9(n_x + n_y - 2n_z) \qquad (1)$$

Au–Cl bond has cylindrical symmetry so $n_x = n_y$. If AuL is a good σ donor then n_z will increase and ν_{Cl} will decrease; if AuL is a good π acceptor then n_x and n_y will decrease and ν_{Cl} will decrease. We also assume that $(n_x + n_y - 2n_z) > 0$; this essentially assigns a secondary importance to π donation in comparison to σ acceptance by the chlorine. It should be noted at this point that in this paper we are discussing the bonding from the point of view of the chlorine atom which 'sees' the AuL moiety as a σ donor and π acceptor; this is the inverse of the usual discussion of metal–ligand bonds, but the same viewpoint used by the organic chemist discussing substituent effects. This approach has advantages when considering the σ-donor and π-acceptor properties of the *trans* ligand L. Given this, the n.q.r. frequency ν_{Cl} is now (2) where A and B are constants

$$\nu_{\text{Cl}} = A - B(\sigma + \pi) \qquad (2)$$

for this series of complexes and σ and π respectively reflect the σ-donor and π-acceptor properties of the AuL moiety.

N.q.r. results for [AuClL] complexes

Ligand	Intensity	$\nu(^{35}\text{Cl})$/MHz					$\left(\frac{\partial\nu}{\partial T}\right)$/kHz K^{-1}
		77	195	273	300	0 K (calc.)	
PEt_3	w [a]	14.34		14.07	14.03	14.44	1.03
		14.71		14.36	14.31	14.85	1.80
$P(C_6H_{11})_3$	vw [a]	14.74		14.43	14.38	14.86	1.60
$P(OMe)_3$	w	14.70	14.61	14.55		14.76	0.77
PPh_3	w [a]	15.33	15.19	15.10	15.11	15.42	1.17
		15.41	15.27	15.17		15.51	1.23
$P(OPh)_3$	m	15.74	15.48	15.28	15.23	15.94	2.67
$AsPh_3$	vw [a]	16.28		15.97	15.93	16.41	1.60
p-$MeOC_6H_4NC$	wm	16.62	16.41	16.27	16.21	16.76	1.80
PhNC	w	16.83	16.62	16.47	16.40	16.98	1.87
SMe_2 [b]	m	16.96	16.78	16.65	16.60	17.09	1.63
$C_6H_{11}NC$	m	17.16	16.90	16.66	16.63	17.38	2.20
PCl_3	w	17.32	17.15	17.04		17.43	1.43
PPh_3S	w	17.67		17.39		17.85	1.4
py	w	17.68	17.48	17.31	17.25	17.85	2.00
		17.96	17.76	17.58		18.13	1.97
Cl^-	w	18.03	17.68	17.43	17.33	18.28	3.10

[a] After heating. [b] ^{37}Cl seen where expected.

The temperature dependence of the n.q.r. frequency varies considerably in the series of complexes studied, although it is always negative. It has been proposed that increasing temperature diminishes the π contribution to the e.f.g. more rapidly than the σ contribution, primarily as a result of the increasing excitation of molecular vibrations, although there are other effects to be considered.[18] If, as a first approximation, we neglect these other effects, then the effect of π bonding is to lower ν_{Cl}; hence its destruction on increasing the temperature will cause ν_{Cl} to decrease less rapidly than in a compound where the bonding is pure σ in character. Thus complexes with the least negative $\partial\nu/\partial T$ will have the highest π-bond character in the AuCl bond, equation (3) where C and D are positive constants.

The results we discuss below do not provide an absolute confirmation of this interpretation of $\partial\nu/\partial T$. They do,

$$\partial\nu/\partial T = -C + D(\pi) \qquad (3)$$

however, show a surprisingly large variation of $\partial\nu/\partial T$ from complex to complex. This variation is generally in accord with the π-acceptor powers of the *trans* ligand L as predicted by chemical intuition.

To permit a quantitative rather than qualitative discussion of our data it is necessary to obtain values for the four constants A—D. A calibration of A and B is possible if it is assumed that Cl^- is a p^6 species and Cl_2 a pure covalent σ-bonded molecule. A calibration for C and D is much harder; a value of D for p_π–d_π bonding in $[MCl_6]^{2-}$ systems was obtained by Kubo and his co-workers.[19] However, the π bonding in [AuClL] complexes is presumably $3p_\pi$–$6p_\pi$ in character and an attempt to use their calibration gave unsatisfactory results. In view of this, and the failure of ν_{Cl} to distinguish σ and π effects, we limit ourselves to a qualitative discussion of the results.

RESULTS AND DISCUSSION

We may take as the starting point for our discussion the complex $[AsPh_4][AuCl_2]$; this has the highest ν_{Cl} implying that Cl^- is the weakest ligand of all those studied. The single resonance seen implies that the two chlorine atoms are equivalent. One would expect no π bonding of the type $\overrightarrow{\text{Cl–Au–L}}$, and any π effects will arise from π donation into the gold $6p_x$ and $6p_y$ orbitals. The ion $[AuCl_2]^-$ has the most negative temperature coefficient, implying the least π bonding in agreement with this. The frequency is much lower than for $[AuCl_4]^-$ (average resonance 28 MHz at 300 K) [20] implying that the

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gold–chlorine bonds are much more ionic in the gold(I) complex, as would be expected. A very crude Townes–Dailey calculation suggests that in $[AuCl_4]^-$ the gold carries a charge of $+1$ and the chlorine $-\frac{1}{2}$, while in $[AuCl_2]^-$ the figures are $+\frac{1}{3}$ and $-\frac{2}{3}$ respectively. By comparison with $[NBu_4][CuCl_2]$ [9.65 (77), and 9.23 MHz (293 K)],[21] the frequency is however much higher, confirming the more covalent nature of gold chemistry.

As the ligand L changes from Cl^- to PEt_3 the n.q.r. frequency of [AuClL] varies by up to 25%. N.q.r. and Mössbauer data for platinum(II) complexes show that for the softer iodine ligand the quadrupole coupling changes even more considerably.[22-24] The order of decreasing ν_{Cl} in the Table is roughly what one could expect for the order of increasing $\sigma + \pi$ effects of the *trans* ligand L, implying that the Au atom transmits this effect fairly directly. ν_{Cl} for the phosphorus ligands falls as the σ-donor power of the substituents on the phosphorus increases from Cl to the groups Et and C_6H_{11}, implying that the *trans* influence of the phosphines is associated mainly with σ effects. The slightly anomalous position of $P(OMe)_3$ in this series may be a result of its strong π-acceptor properties (see below).

There are however certain differences from the $\sigma + \pi$ effects of ligands measured by the partial chemical shift parameter applied to iron(II) compounds,[25,26] notably for the isocyanides which, in iron(II) complexes, appear to be much stronger ligands. For Au^I they are roughly similar in strength to SMe_2 and much weaker than the phosphines. This effect is also found, although to a lesser extent, in the ^{197}Au Mössbauer spectra of these complexes and in the greater instability of $[IrL_4]^+$ when L is an isocyanide rather than a phosphine.[27,28] The correlation with the position of L in the spectrochemical series (which is also a measure of its σ-donor and π-acceptor properties) is also poor, the phosphines again appearing rather too strong as ligands. The order of ligands cannot be a measure of the softness of the ligating atom as the sulphur-containing ligands are much weaker than the phosphines, and ν_{Cl} for the phosphines is strongly dependent on the atoms bonded to the phosphorus, an effect transmitted through two intervening atoms. There is no correlation between ν_{Cl} and Au–Cl stretching frequencies.[10]

The π-bonding effects, as shown by $\partial\nu/\partial T$, are also generally in accord with predictions: $P(OMe)_3 > PPh_3 > PPh_3S \sim PCl_3 \sim PEt_3 > P(C_6H_{11})_3 \sim AsPh_3 \sim SMe_2 > p\text{-}MeOC_6H_3NC > PhNC > py > C_6H_{11}NC > P(OPh)_3 > Cl^-$. Phosphines are expected to be stronger than arsines, and sulphides would also be expected to be weak π acceptors. Changing substituents on the phosphine also shows the expected behaviour. Electron-withdrawing species such as Ph, Cl, and MeO show much stronger acceptance as might be expected, and the strong acceptor properties of $P(OMe)_3$ are in accord with the Mössbauer results of Bancroft.[25] The isocyanides also show a reasonable substituent effect in their π acceptance: $p\text{-}MeOC_6H_4NC > PhNC > C_6H_{11}NC$. ν_{Cl} decreases in the same sense as increasing π acceptance, and in the opposite sense to the increasing σ-donation effects of the substituent on the isocyanide; it is thus possible that π acceptance is important for these isocyanide ligands.

These observations support the π-bonding interpretation of the temperature coefficient. However, there are two complexes which give surprising results: the high-temperature coefficient for $[AuCl\{P(OPh)_3\}]$, and the two different coefficients for the two sites found in $[AuCl(PEt_3)]$. The second may be due to intermolecular bonding involving one of the inequivalent chlorine sites which can drastically affect the temperature dependence of an n.q.r. line, as was found for $Na[AuCl_4]\cdot 2H_2O$.[20] It seems that the temperature coefficient is a useful, but not 100% reliable, measure of the π bonding.

Previous Quadrupole-coupling Studies.—A paper on chlorine n.q.r. of platinum(II) square-planar complexes,[20] and three on ^{129}I Mössbauer of platinum(II) complexes have already appeared.[22-24] The general order of iodine quadrupole couplings is the same as for the chlorine complexes, although as Dale *et al.*[22] pointed out the percentage changes are greater for the softer iodide ligands. These systems suffer from the disadvantage that it is impossible to ignore the *cis* effect, which appears to be quite considerable for these complexes.

The simplest comparison is with the results of Bancroft and Butler [24] where in the complex *trans*-$[PtIL(PMe_2Ph)_2]$ the *trans* ligand L is varied. The correlation with our ν_{Cl} values is very poor, the frequency for $L = PPh_3$ being far too high and for EtNC far too low; however, the values for I^-, $AsPh_3$, $P(OMe)_3$, and p-$MeOC_6H_4NC$ are at least roughly in agreement. For the *cis*-$[PtX_2L_2]$ complexes studied, even this correlation disappears,[20,23] the complexes with L = py having lower frequencies than those with phosphine ligands. There are two likely reasons for this discrepancy. (1) There is always a *cis* influence present in these platinum complexes comparable in magnitude to and opposed to the *trans* influence.[22] (2) In the gold(I) complexes the metal orbitals involved are the 6*s* and 6*p*, while for platinum(II) complexes the $5d_{x^2-y^2}$ must also be considered. The Mössbauer evidence discussed in the following paper rules out any great involvement of the $5d_{z^2}$ orbital in the gold(I) complexes.

In view of this, and the complexity of the platinum(II) results, it seems inadvisable to attempt detailed comparison with these results and we note only that the order of the *trans*-influence power of the ligands seems rather

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different. As Clark and his co-workers pointed out,[1] different methods of measuring the effect generally give slightly different orders of *trans* influence. Paradoxically, our results agree better with the order obtained by methods of measurement other than n.q.r., being reasonably in accord with those obtained by n.m.r. coupling constants and bond-length studies.

Conclusions.—Our qualitative discussion of the *trans* influence has shown that the stronger the *trans* ligand the lower ν_{Cl}, implying a significant change in the Au–Cl bond. The σ *trans* influence appears to be more important than π effects in most of the complexes studied. The order of the *trans* influence is not particularly surprising, although it does show significant differences from the bonding properties predicted by ^{57}Fe Mössbauer and electronic spectroscopy.

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