Gold-197 Mössbauer Spectra of Organogold(I) Compounds

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Gold-197 Mössbauer parameters are reported for the salts $Z[AuR_2]$ {R = C_6F_5, Z = $[NBu_4]^+$, $[Ag(C_4H_8S)]^+$, $[Au(SbPh_3)_4]^+$, or $[Au(pdma)_2]^+$ [pdma = *o*-phenylenebis(dimethylarsine)]; R = $C_6F_3H_2$, Z = $[NBu_4]^+$, Ag^+, or $[Ag(C_4H_8S)]^+$}. For salts of the same cation, the isomer shift and quadrupole splitting are both slightly smaller for R = C_6F_5 than for R = $C_6F_3H_2$, in accord with the electronegativities of the aryl groups. For each anion, the parameters decrease in the order Z = $[NBu_4]^+$ > $[Ag(C_4H_8S)]^+$ > Ag^+; this trend probably indicates increasing interionic association. The data for the two gold-containing cations are consistent with four co-ordination; the lower symmetry of $[Au(pdma)_2]^+$ is revealed by a small quadrupole splitting. These cations give more intense spectra than the anions, consistent with dependence of the recoil-free fraction on ionic mass.

Mössbauer spectroscopy has proved to be a powerful technique for the characterisation of gold compounds. The two major oxidation states can be readily distinguished, and for each oxidation state there is a systematic relationship between the spectroscopic parameters and the number and nature of the ligands.[1,2] Unfortunately, few data are available for organic derivatives of gold(I). The only simple complexes which appear to have been examined by the Mössbauer method are phosphine complexes of methylgold, $[AuMe(PR_3)]$ (R = Me or Ph),[3,4] and the ylide derivatives $[Au_2(\mu\text{-}CH_2PEt_2CH_2)_2]$.[5] Data for compounds of composition $LiAu(C_6H_4Y)_2$, $CuAu(C_6H_4Y)_2$, and $Cu_2AuX(C_6H_4Y)_2$ have been reported (Y = NMe_2 or CH_2NMe_2; X = I or O_3SCF_3),[6-8] but these materials are dimeric clusters involving three-centre two-electron bonds. In order to extend the range of data available, and to consolidate the correlations mentioned above, we have examined salts of the anions $[Au(C_6F_5)_2]^-$ and $[Au(C_6F_3H_2)_2]^-$ with the cations $[NBu_4]^+$, Ag^+, $[Ag(C_4H_8S)]^+$ (C_4H_8S = tetrahydrothiophene), $[Au(SbPh_3)_4]^+$, and $[Au(pdma)_2]^+$ [pdma = *o*-phenylenebis(dimethylarsine)]. The crystal structures of three of these compounds have recently been reported.[9-11]

Results and Discussion

The new Mössbauer data are given in Table 1, together with those available for other organogold(I) compounds. For $[Au(SbPh_3)_4][Au(C_6F_5)_2]$ and $[Au(pdma)_2][Au(C_6F_5)_2]$, signals for the two types of gold atom can be distinguished: the cations give intense signals with isomer shifts (i.s.) of *ca.* 1.0 mm s^{-1}, while the anions give much weaker doublets, the low-velocity lines of which are obscured by the cation absorption. In each case, the higher-velocity line was in almost the same position (within 0.3 mm s^{-1}) as that for $[NBu_4][Au(C_6F_5)_2]$, and it is assumed that the parameters are similar to those of the latter salt.

The marked difference in intensity between the signals for the cations and anions presumably reflects a difference in the recoil-free fraction (f) between the ions, which must be due principally to their difference in mass. Trooster and coworkers[12] have shown that, for related compounds, the logarithm of f is inversely related to the molar mass. On this basis, the relative spectrum areas for $[Au(C_6F_5)_2]^-$, $[Au(pdma)_2]^+$, and $[Au(SbPh_3)_4]^+$ should be approximately 1 : 2.1 : 5.3. The observed ratios are rather less than this (*ca.* 1 : 1.5 and *ca.* 1 : 3.5), which may indicate a different dependence of f on mass for two-co-ordinate and four-co-ordinate systems. Other things being equal, the shorter and, presumably, stronger bonds in two-co-ordinate systems would lead to higher f values.

The Cations.—Both $[Au(pdma)_2]^+$ and $[Au(SbPh_3)_4]^+$ are known to be four-co-ordinate,[10,11] and the Mössbauer parameters are consistent with this. The isomer shifts are extremely low and lie in the range observed for other four-co-ordinate complexes (-0.4 to $+2.0$ mm s^{-1}, see Table 2). The lack of observable quadrupole splitting (q.s.) indicates structures close to tetrahedral. In $[Au(SbPh_3)_4]^+$ the bond angles are regular, but there is some variation in the bond lengths (259—267 pm).[11] Such a slight distortion has no discernible effect on the Mössbauer spectrum, and a single line of normal width is seen. The $[Au(pdma)_2]^+$ salt gives a much broader line (*ca.* 2.8 mm s^{-1}), which can be fitted as a doublet with q.s. *ca.* 1.1 mm s^{-1}. In this cation, the small bite of the chelating ligand gives a distorted tetrahedral geometry with As–Au–As bond angles of 87 and 122°,[10] and produces a non-zero electric-field gradient (e.f.g.) at the gold nucleus.

The Anions.—For two-co-ordinate systems there is a well established relationship between i.s. and q.s., both parameters increasing with increasing donor power of the ligands.[1,2] For σ-bonded organic ligands, high values of the parameters are expected; the values observed here are among the highest recorded, but lie within the band of values associated with two-co-ordinate species (see Figure). The data for previously measured organogold(I) compounds, including most of the electron-deficient compounds, also lie within the band. The parameters reported for $Au(C_6H_4Y)$ (Y = NMe_2 or CH_2NMe_2) fall well below the other data; these compounds are thought to be polymeric with multi-centre bonds,[8] but the Mössbauer parameters resemble those for gold(III) compounds.[1,2]

The parameters for the fluoro-aryl derivatives show a systematic variation with the cation, decreasing in the order $[NBu_4]^+$ > $[Ag(C_4H_8S)]^+$ > Ag^+. There is a considerable parallel with van Koten's compounds[6-8] $[Z_2Au_2(C_6H_4Y)_4]$, where the i.s. and q.s. decrease in the order Z = Li > Cu > Cu_2X (X = I or O_3SCF_3), and detailed comparisons are made below. These variations in parameters reflect interactions between the anion and cation, and similar changes are seen in other systems involving such interactions, *e.g.* salts of the $[AuCl_2]^-$ and $[AuCl_4]^-$ ions (see Table 3).

There appear to be no interionic interactions affecting the

Table 1. Gold-197 Mössbauer data for organogold(I) compounds

	No. in Figure	i.s.[a,b]/ mm s^{-1}	q.s.[b]/ mm s^{-1}	Linewidths [c]/ mm s^{-1}	Ref.
$[NBu_4][Au(C_6F_5)_2]$	2	5.37	10.70	1.95, 2.12	*d*
$[Au(SbPh_3)_4][Au(C_6F_5)_2]$ cation		1.11	0.0	2.04 [e]	*d*
anion		*ca.* 5.4 [f]	*ca.* 10.5 [f]	2.04 [e]	
$[Au(pdma)_2][Au(C_6F_5)_2]$ cation		0.8	1.1	1.93 [g]	*d*
anion		*ca.* 5.3 [f]	*ca.* 10.5 [f]	2.48 [g]	
$[Ag(C_4H_8S)][Au(C_6F_5)_2]$	4	4.59	9.23	1.93, 2.20	*d*
$[NBu_4][Au(C_6F_3H_2)_2]$	1	5.47	10.92	2.37, 2.12	*d*
$[Ag(C_4H_8S)][Au(C_6F_3H_2)_2]$	3	4.57	9.41	1.91, 2.14	*d*
$Ag[Au(C_6F_3H_2)_2]$	5	3.98	8.63	1.95, 2.17	*d*
$[Au(Me)(PPh_3)]$	11	6.14	10.35		3
$[Au(Me)(PMe_3)]$	12	6.11	10.21		4
$[Au(C_6H_4NMe_2\text{-}2)(PPh_3)]$	13	6.05	10.11		8
$[Au(C_6H_4CH_2NMe_2\text{-}2)(CNC_6H_{11})]$	14	5.83	10.35		8
$[Au_2(\mu\text{-}CH_2PEt_2CH_2)_2]$	15	4.97	9.60		5
$[\{Au(C_6H_4NMe_2\text{-}2)\}_n]$		4.90	6.73		8
$[\{Au(C_6H_4CH_2NMe_2\text{-}2)\}_n]$		5.64	7.32		8
$[Li_2Au_2(C_6H_4NMe_2\text{-}2)_4]$	6	6.86	12.01		6
$[Li_2Au_2(C_6H_4CH_2NMe_2\text{-}2)_4]$	7	6.48	11.29		8
$[Cu_2Au_2(C_6H_4NMe_2\text{-}2)_4]$	8	5.63	9.86		8
$[Cu_4Au_2I_2(C_6H_4NMe_2\text{-}2)_4]$	9	5.21	9.37		7
$[Cu_4Au_2(O_3SCF_3)_2(C_6H_4NMe_2\text{-}2)_4]$	10	5.09	9.14		7

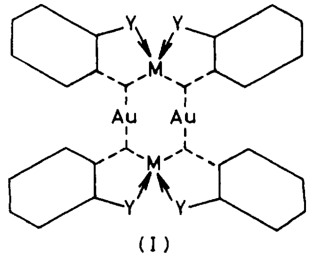
[a] Relative to gold metal. [b] ±0.05 mm s^{-1}. [c] ±0.10 mm s^{-1}. [d] This work. [e] All three linewidths constrained to be equal. [f] See text. [g] Widths constrained.

Table 2. Gold-127 Mössbauer data for four-co-ordinate gold(I) complexes

	i.s.[a]/ mm s^{-1}	q.s./ mm s^{-1}	Ref.
$[Au(AsPh_3)_4]ClO_4$	−0.39	0.0	19
$[Au(PPh_3)_4]ClO_4$	−0.17	0.0	*b*
$[Au(PMePh_2)_4]ClO_4$	1.48	0.0	19
$[Au(PMe_2Ph)_4]BPh_4$	1.98	0.0	*c*
$[Au(SnCl_3)(PPh_3)_3]$	1.64	3.57	20
$[AuCl(PPh_3)_3]$	1.18	4.38	*d*

[a] Relative to gold metal. [b] R. V. Parish and J. D. Rush, *Chem. Phys. Lett.*, 1979, **63**, 37. [c] A. K. H. Al-Sa'ady, K. Brown, R. V. Parish, and C. A. McAuliffe, Proc. Int. Conf. Applications Mössbauer Effect, Jaipur, India, Indian Nat. Acad. Sci., New Delhi, 1982, p. 723. [d] A. K. H. Al-Sa'ady, K. Moss, R. V. Parish, and C. A. McAuliffe, unpublished work.

gold atoms in $[Au(pdma)_2][Au(C_6F_5)_2]$,[10] and the same is presumably true of the $[Au(SbPh_3)_4]^+$ and $[NBu_4]^+$ salts. For the compounds $[NBu_4][AuR_2]$ both i.s. and q.s. increase slightly from R = C_6F_5 to R = $C_6F_3H_2$, as would be expected from the relative electronegativities of the aryl groups. The Li-C_6H_4Y (Y = NMe_2 or CH_2NMe_2) derivatives show larger values for both parameters, consistent with a further decrease in electronegativity. These last compounds are, however, not simple salts, $Li[Au(C_6H_4Y)_2]$, but have a dimeric cluster structure in which the aryl groups bridge between gold and lithium atoms in three-centred two-electron bond systems [see structure (I); M = Li].[6] The possibility that dimerisation occurs simply by co-ordination of the amino-groups to lithium is excluded by the observation in the ^{13}C n.m.r. spectrum of spin–spin coupling between the lithium and bridging carbon atoms.[6] The coupling constant (*ca.* 7 Hz) is much lower than those observed in the lithium alkyls (10—15 Hz),[13,14] which suggests that the contribution of the Li 2*s* orbital to the three-centre bond system is small; there is presumably a correspondingly larger contribution from the 6*sp* hybrid of the gold atom. The electron density in the



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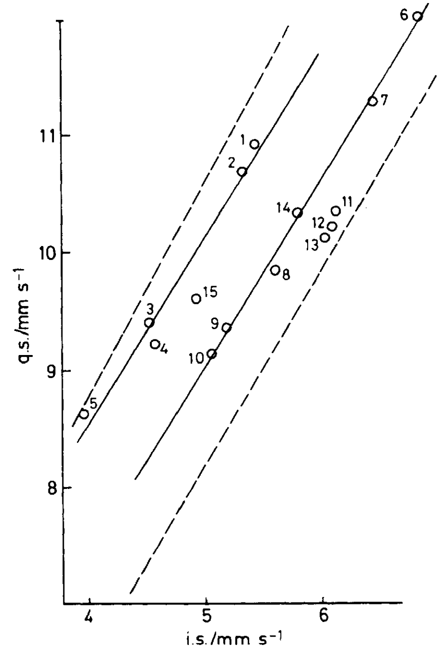


Figure. Isomer shift/quadrupole splitting correlation diagram for organogold(I) complexes. The numbering of points corresponds to Table 1. The two full lines are least-squares fits through points 1—5 and 6—10. The broken lines are the boundaries of the two-co-ordination correlation band (ref. 1)

Table 3. Gold-197 Mössbauer data for salts with cation–anion interaction

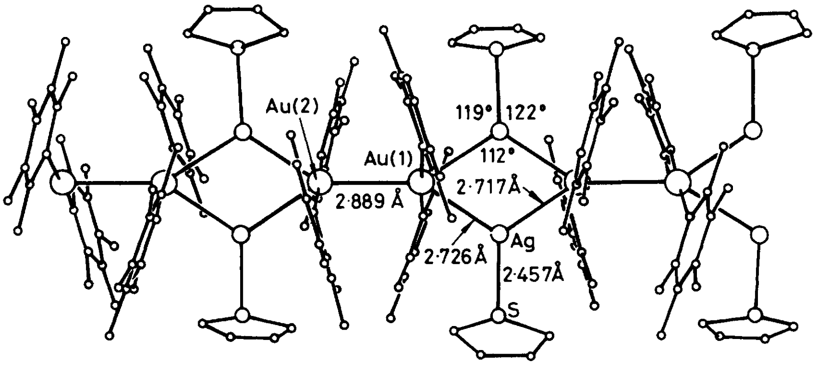
	i.s.[a]/ mm s^{-1}	q.s./ mm s^{-1}	Ref.
$Cs_2[AuCl_2][AuCl_4]$ [b]	0.10	4.93	*c*—*e*
$[AuCl_2(C_7H_8)][AuCl_2]$ [b]	0.83	4.00	*f*
$[Au(H_2dmg)_2][AuCl_2]$ [b,g]	1.58	6.03	*e*
$[AsPh_4][AuCl_2]$	1.72	6.13	*h*
$[Au(S_2CNBu_2)_2][AuCl_2]$ [b]	1.95	6.43	12
$[Au(S_2CNPh_2)_2][AuCl_2]$ [b]	2.26	6.35	12
$H[AuCl_4]\cdot 4H_2O$	1.87	0.94	*i*
$Na[AuCl_4]\cdot xH_2O$	2.02	1.30	7, *i*
$K[AuCl_4]\cdot xH_2O$	1.92	1.26	7, *c*, *i*
$Cs[AuCl_4]$	2.16	1.37	*g*
$[NH_4][AuCl_4]\cdot xH_2O$	2.08	1.45	7
$[NBu_4][AuCl_4]$	2.23	1.31	7
$[AsPh_4][AuCl_4]$	2.30	1.88	7
$[EtNC_5H_5][AuCl_4]$	2.23	1.4	7

[a] Relative to gold metal. [b] Data for $[AuCl_2]^-$ only. [c] M. O. Faltens and D. A. Shirley, *J. Chem. Phys.*, 1970, **53**, 4249. [d] J. Stanek, *J. Chem. Phys.*, 1982, **76**, 2315. [e] M. Katada, Y. Uchida, K. Sato, H. Sano, H. Sakai, and Y. Maeda, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 444. [f] H. D. Bartunik and G. Kaindl, in ' Mössbauer Isomer Shifts,' eds. G. K. Shenoy and F. E. Wagner, North-Holland, New York, 1978, p. 535. [g] H_2dmg = dimethylglyoxime. [h] P. G. Jones, A. G. Maddock, M. J. Mays, M. M. Muir, and A. F. Williams, *J. Chem. Soc., Dalton Trans.*, 1977, 1434. [i] H. D. Bartunik, W. Potzel, R. L. Mössbauer, and G. Kaindl, *Z. Phys.*, 1970, **240**, 1.

multi-centre bonds is thus concentrated in the Au–C region, so that the environment of the gold atoms approximates to that for discrete $[Au(C_6H_4Y)_2]^-$ anions.

The copper derivatives $[Cu_2Au_2(C_6H_4Y)_4]$ ($Y = NMe_2$) have analogous structures (I; M = Cu).[8] The introduction of a Cu^+ ion into the three-centre two-electron bond system in place of Li^+ would be expected to polarize the electron distribution towards the copper atom and away from the gold atom, and this is reflected in the lower i.s. and q.s. values. In the hexanuclear compounds $[Cu_4Au_2X_2(C_6H_4Y)_4]$ ($Y = NMe_2$; X = I or O_3SCF_3), the metal atoms are thought to define a *trans*-Au_2Cu_4 octahedron in which the two gold atoms are linked by bridging aryl groups to different pairs of copper atoms.[15] The local environment of the gold atoms is thus very similar to that in the dicopper compounds. However, each copper atom is also bonded to a (bridging) electronegative ligand (I^- or $CF_3SO_3^-$), which increases its effective electronegativity, and results in a further withdrawal of 6*sp* electron density from the gold atom.

As evidenced by the trend in Mössbauer parameters, a similar withdrawal of 6*sp* electron density occurs in the Ag^+ and $[Ag(C_4H_8S)]^+$ salts of $[AuR_2]^-$ ($R = C_6F_3H_2$ or C_6F_5), but in these cases the aryl groups are terminal ligands and are not involved in bridging. The crystal structure of $[Ag(C_4H_8S)][Au(C_6F_5)_2]$ shows linear $[Au(C_6F_5)_2]^-$ anions associated in pairs and linked to adjacent pairs by two $[Ag(C_4H_8S)]^+$ cations [structure (II)].[9] The Au–Au and Au–Ag contacts are extremely short (2.889 and 2.726 Å respectively), and indicate metal–metal interactions,[16] so that the gold atoms have an effectively trigonal-bipyramidal environment. The structure of $Ag[Au(C_6F_5)_2]$ is not known, but may well be analogous. In these cases, electron density must be withdrawn from the gold atoms to form delocalised metal–metal bonds. It was originally suggested[9] that this system involved donation of 5*d* electron density from the gold to the silver atoms, but this is not consistent with the Mössbauer data. Reduction in the 5*d* electron density would be expected to increase the i.s. and also to affect the q.s. The principal (*z*) component of the e.f.g. presumably lies in C–Au–C direction, and is negative. Withdrawal of electron density from the *x*–*y* plane would give a further negative contribution to the e.f.g. and an increase in q.s. In fact, both parameters decrease.



(II)

Recent studies[17,18] show that participation of the Au 5*d* orbitals in the bonding of gold(I) compounds is small, and it is more likely that the metal–metal interactions involve the 6*s* and 6*p* orbitals. It is therefore suggested that the gold atom undergoes a rehybridisation with increase in the population of $6p_x$ and $6p_y$ orbitals at the expense of 6*s* and $6p_z$ but without significant involvement of 5*d* electrons. The linear geometry of the anion suggests that the populations of $6p_x$ and $6p_y$ are approximately equal, *i.e.* that the Au–Au and Au–Ag bonding interactions are equivalent, and the in-plane hybridisation approximates to sp^2. Rehybridisation of this type would decrease the e.f.g. at the gold nucleus, by reduction in the *p* imbalance, and would also decrease the i.s. by depopulation of 6*s* and by an increase in the shielding by 6*p* electrons. The removal of electron density from the sp_z hybrids might be expected to weaken the Au–C bonds, but there is no discernible change in the bond lengths.[9-11] The rehybridisation would presumably be greater for a ' bare ' Ag^+ cation than for the thiophene-co-ordinated cation $[Ag(C_4H_8S)]^+$, in accord with the further decrease in i.s. and q.s.

The metal–metal interactions raise the effective co-ordination number of the gold atom. In other systems, such interactions result in decreases in isomer shift.[1,2,19-21] Compounds in which the gold atom makes three full two-centre two-electron bonds have parameters which lie completely outside the two-co-ordination correlation band of the Figure. Other systems, in which the addition interactions are weaker, such as $[Au(SnCl_3)(PMe_2Ph)_2]$ and $[AuX(PEt_3)_2]$ ($X = Cl$, I, or SCN) and, more relevant to the present discussion, the Au_n ($n = 8, 9, 11$, or 55) cluster compounds, give parameters which lie on the low-i.s. edge of the correlation band.[1,2] The data for the fluoro-aryl compounds also lie on the low-i.s. edge (Figure). The excellent linear i.s.–q.s. correlation for the fluoro-aryl compounds may imply some metal–metal interaction even in the $[NBu_4]^+$ salt.

Experimental

The compounds were prepared as previously described.[9–11] Mössbauer measurements were made with source (Au/Pt) and absorber immersed in liquid helium by methods previously described.[18]

Acknowledgements

We are grateful to the S.E.R.C. for the award of a Studentship (to K. M.) and to Professor C. E. Johnson for the loan of a ^{196}Pt source.

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Received 10*th January* 1983; *Paper* 3/037