^{197}Au Mössbauer Spectra of Complexes of Bis(diphenylphosphino)amine containing Gold(I), Gold(II), and Gold(III)

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Gold-197 Mössbauer spectra are reported for previously described complexes of bis(diphenylphosphino)amine (dppa) with gold(I) and gold(II), including those containing perhalogenoaryl ligands. A gold(I + III) complex is reformulated on the basis of its spectrum. The data for all gold(II) complexes are discussed in terms of the bonding and electron configurations.

Gold complexes with short-chain bridging ligands such as (**1**) or (**2**) provide interesting chemical possibilities. In addition to symmetrical digold(I) and digold(III) complexes of types (**3**)—(**6**),[1–5] an intermediate stage of oxidation can often be obtained.[2,3,5] Similar derivatives are known with bridging ylide ligands.[6–11] However, the distinction between mixed-oxidation-state gold(I + III) (**7**) and (**8**) and true gold(II + II) systems (**9**) and (**10**) is not easy. Definitive characterisation by *X*-ray crystallography has been possible in many instances,[1,3–11] and ESCA (electronic spectroscopy for chemical analysis)[2,12] or Mössbauer spectroscopy[2,3,12] has also been used. The latter technique is particularly valuable, since complexes of gold(I) and gold(III) usually have quite distinct parameters,[13–15] and both sets of signals should be plainly discernible in gold(I + III) spectra. This has been demonstrated in the case of a complex of structure (7; Y = CH_2).[2] In addition, the values of the Mössbauer parameters vary systematically with the nature of the ligands, so that co-ordination isomers can be distinguished.

We report now on the Mössbauer spectra of some complexes of ligand (**2**; R = H), bis(diphenylphosphino)amine (dppa), which show all these features. The syntheses of the majority of the complexes have been described previously.[5]

Experimental

Mössbauer spectra were obtained by standard methods, with both source and sample immersed in liquid helium.[16] Isomer shifts are quoted relative to metallic gold at 4.2 K.

[R(I)Au(dppa)Au(I)R] (R = C_6F_5 *or* C_6Cl_5).—To a dichloromethane solution (10 cm^3) of iodine (25.2 mg, 0.10 mmol) was added [RAu(dppa)AuR] (0.10 mmol). A violet precipitate appeared immediately and was collected. Vacuum concentration of the filtrate and addition of n-hexane afforded further material. Overall yield, 65% [Found (R = C_6F_5): C, 31.4; H, 1.65; Au, 28.0; N, 0.9. Calc. for $C_{36}H_{21}Au_2F_{10}I_2NP_2$: C, 31.6; H, 1.55; Au, 28.8; N, 1.00. Found (R = C_6Cl_5): C, 28.65; H, 1.50; Au, 25.4; N, 1.20. Calc. for $C_{36}H_{21}Au_2Cl_{10}I_2NP_2$: C, 28.2; H, 1.40; Au, 25.7; N, 0.90%].

Results

The parameters for the gold(I) complexes [ClAu(dppa)AuCl], $[Au_2(dppa)_2]^{2+}$, and [(C_6F_5)Au(dppa)Au(C_6F_5)] (Table 1) are consistent with previously recorded data for compounds with Cl–Au–P, P–Au–P, and P–Au–R co-ordination (R = fluorinated organic group), representative examples of which are included in the Table.

Gold(II) complexes of general formula [R(X)Au(dppa)-Au(X)R] (X = Cl, Br, or I; R = C_6F_5 or C_6Cl_5) gave simple doublet spectra, with no indication of any asymmetry. The parameters (Table 2) are very similar to those of the ylide complex $[(BrAuCH_2PEt_2CH_2)_2]$, which also contains gold(II) co-ordinated to soft ligands and one halide, and structure (**9**) can safely be assigned, as found by *X*-ray crystallography for R = C_6F_5, X = Cl.[5] Two complexes which were thought to be $[(R)Au(dppa)Au(R)I_2]$ (R = C_6F_5 or C_6Cl_5) gave Mössbauer spectra with parameters very similar to those of [(R)IAu-(dppa)AuI(R)].

The complexes $[Au_2(dppa)_2X_2][ClO_4]_2$ (X = Cl or Br) gave complicated spectra which plainly contained more peaks than expected for the simple gold(II + II) formulation (**10**). To obtain reasonable fittings, it was necessary to include three doublets in each spectrum (Figure 1). Since the doublets were heavily overlapped, it was also necessary to constrain the widths of all six lines to be equal. Assignments were made in such a way that the parameters corresponded to chemically reasonable species. For both samples, one doublet, (A), has parameters slightly greater than those of [R(X)Au(dppa)Au(X)R], and is consistent with a gold(II + II) formulation of type (**10**). A second doublet, (B), has parameters somewhat lower than for the gold(II) species, but the quadrupole splitting (q.s.) shows considerably greater diminution than the isomer shift (i.s.), suggesting that the oxidation state is different, probably, therefore, gold(III). These parameters lie almost halfway between those for $PAu^{III}X_3$ and $PAu^{III}R_3$, and are slightly lower than for $PAu^{III}R_2X$. A reasonable assignment is therefore $P_2Au^{III}X_2$, as in (**6**) or (**8**). The third doublet corresponds to gold(I) with PAuX co-ordination. There is no evidence for PAu^IP species, so that structure (**8**) can be ruled out. The parameters are significantly different from those of [ClAu-(dppa)AuCl], and possible formulations are [Au(dppa)Cl] and $[\{Au(ClO_4)\}_2dppa]$; in view of the low parameters, the latter, with PAuO co-ordination, seems more likely.

Similar problems were encountered with a product of composition $Au_2(dppa)Cl_2(C_6F_5)_2$. The spectrum was very broad, indicating the presence of two poorly resolved doublets for which only one satisfactory solution was possible. The parameters were consistent with PAu^ICl (4.01, 7.50 mm s^{-1}) and $PAu^{III}Cl(C_6F_5)_2$ (5.24, 6.82 mm s^{-1}). The presence of $PAu^I(C_6F_5)$ could be definitely discounted, since no absorption was evident at *ca.* 10.1 mm s^{-1}, the position of the high-velocity line of [(C_6F_5)Au(dppa)Au(C_6F_5)].

Discussion

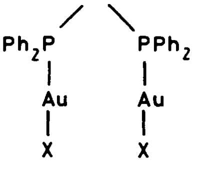
The parameters for gold(I) complexes of dppa (Table 1) are consistent with the large body of data already available for two-

$Ph_2P{-}CR_2{-}PPh_2$

(1)

$Ph_2P{-}NR{-}PPh_2$

(2)



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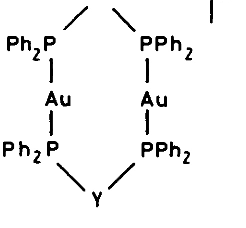

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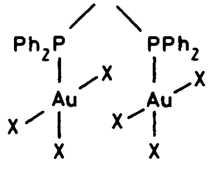

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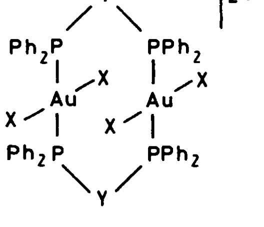

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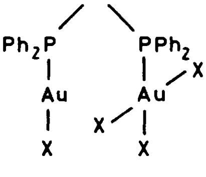

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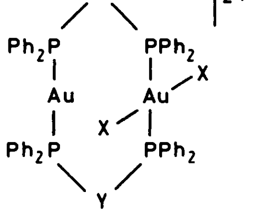

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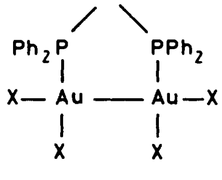

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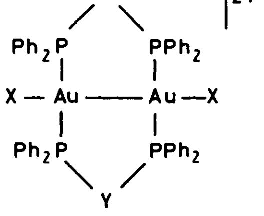

(10)

Table 1. ^{197}Au Mössbauer data for gold(I) complexes

	I.s.	Q.s.	Linewidth	
Complex		mm s^{-1}		Ref.
[ClAu(dppa)AuCl]	3.91	7.06	2.12, 2.04	*a*
[ClAu($Ph_2PCH_2PPh_2$)AuCl]	3.73	7.03		12
	3.75	7.17		2
[ClAu(cdppen)AuCl]^{b}	3.42	6.94		*c*
[Au(tdppen)Cl]^{d}	3.73	7.46		*c*
$[Au_2(dppa)_2][ClO_4]_2$	4.93	8.98	1.91, 2.28	*a*
$[Au(PMePh_2)_2]ClO_4$	4.92	9.38		*c, e*
$[(C_6F_5)Au(dppa)Au(C_6F_5)]$	5.20	9.91	1.93, 2.16	*a*
$[(Me_3P)Au(thfbd)AuMe_2(PMe_3)]$^{f,g}	5.58	9.18		*h*
$[(Me_3)PAu(chfbd)AuMe_2(PMe_3)]$^{f,i}	5.35	9.17		*h*
$[(PhMe_2P)Au(chfbd)AuMe_2(PMe_2Ph)]$^{f,i}	5.64	9.44		*h*
$[AuMe(PPh_3)]$	6.14	10.35		*j*

[a] This work. [b] cdppen = *cis*-$Ph_2PCH{=}CHPPh_2$. [c] C. A. McAuliffe, R. V. Parish, and P. D. Randall, *J. Chem. Soc., Dalton Trans.*, 1977, 1426. [d] tdppen = *trans*-$Ph_2PCH{=}CHPPh_2$. [e] P. G. Jones, A. G. Maddock, M. J. Mays, M. M. Muir, and A. F. Williams, *J. Chem. Soc., Dalton Trans.*, 1977, 1434. [f] Data for gold(I) atom only. [g] thfbd = *trans*-$C(CF_3){=}C(CF_3)$. [h] J. A. Jarvis, A. Johnson, and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, 1973, 373. [i] chfbd = *cis*-$C(CF_3){=}C(CF_3)$. [j] J. S. Charlton and D. J. Nicholls, *J. Chem. Soc. A*, 1970, 1484.

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co-ordinate gold(I). Comparison with [AuCl(L)] and $[AuL_2]^+$ (L = $PMePh_2$ or $PEtPh_2$) shows that dppa has very similar donor properties (to gold) to these two monodentate ligands, *i.e.* that the central amine group has little effect on the donor properties of the phosphine groups. The significantly lower i.s. and q.s. of $[(C_6F_5)Au(dppa)Au(C_6F_5)]$ than of $[AuMe(PPh_3)]$ is a reflection of the relatively high electronegativity of the perfluoroaryl group. The calculated partial quadrupole splitting (p.q.s.) parameter for C_6F_5 is −2.71 mm s^{-1} compared to −2.80, −2.82, and −3.00 mm s^{-1} for Me, 2-$Me_2NC_6H_4$, and 2-$Me_2NCH_2C_6H_4$ groups, respectively. As with other gold(I) complexes, the spectroscopic parameters give no information about the presence or absence of short gold–gold interactions.[17]

The mixed-valence gold(I + III) complex $[Au_2(dppa)Cl_2(C_6F_5)_2]$ appears to be $[ClAu^{I}(dppa)Au^{III}Cl(C_6F_5)_2]$, which differs from the assignment originally made on the basis of the i.r. spectrum,[5] and demonstrates the value of the Mössbauer method in distinguishing between possible isomers. The relative intensities of the sub-spectra are in the ratio 2:1 (Au^{III}:Au^{I}), which indicates different recoil-free fractions(*f*) for the two gold sites. It has been shown that, for co-ordination complexes of gold, there are approximate linear correlations

Table 2. ^{197}Au Mössbauer data for gold(II) and gold(III) complexes

Complex	I.s.	Q.s.	Linewidth	Ref.
	mm s^{-1}			
Gold(II)				
$[(C_6F_5)ClAu(dppa)AuCl(C_6F_5)]$	4.19	6.47	3.23, 2.12	*a*
$[(C_6Cl_5)ClAu(dppa)AuCl(C_6Cl_5)]$	4.20	6.20	2.37, 2.10	*a*
$[(C_6F_5)BrAu(dppa)AuBr(C_6F_5)]$	4.11	6.52	2.48, 2.39	*a*
$[(C_6Cl_5)BrAu(dppa)AuBr(C_6Cl_5)]$	4.22	6.26	2.52, 2.27	*a*
$[(C_6F_5)IAu(dppa)AuI(C_6F_5)]$	4.30	6.59	2.29, 2.07	*a*
$[(C_6Cl_5)IAu(dppa)AuI(C_6Cl_5)]$	4.20	6.56	2.14, 2.30	*a*
$[Au_2(dppa)_2Cl_2][ClO_4]_2$	(A) 4.62	7.95		
	(B) 4.36	6.09	2.01	*a*
	(C) 3.32	6.79		
$[Au_2(dppa)_2Br_2][ClO_4]_2$	(A) 4.60	7.68		
	(B) 4.41	5.95	2.01	*a*
	(C) 3.29	6.72		
$[(BrAuCH_2PEt_2CH_2)_2]$	3.88	6.71		12
$[Cl_2Au(Ph_2PCMe_2PPh_2)AuCl_2]$	3.22	3.70		2
$[ClBrAu(Ph_2PCMe_2PPh_2)AuClBr]$	3.22	3.58		2
$[Cl_2Au(Ph_2PNMePPh_2)AuCl_2]$	3.66	4.20		3
Gold(III)				
$[(PhMe_2P)Me_2Au(thfbd)Au(PMe_2Ph)]^{b,c}$	6.32	9.13		*d*
$[(Me_3P)Me_2Au(thfbd)Au(PMe_3)]^{b,c}$	6.37	9.22		*d*
$[(Me_3P)Me_2Au(chfbd)Au(PMe_3)]^{b,e}$	6.49	9.07		*d*
$[AuClMe_2(PPh_3)]$	5.28	6.32		*f*
$[AuClMe_2(PMePh_2)]$	5.27	6.33		*f*
$[AuBrMe_2(PMePh_2)]$	5.38	6.30		*f*
$[AuMe_3(PPh_3)]$	5.91	8.57		*f*
$[ClBr_2Au(Ph_2PCH_2PPh_2)AuBr]^{b}$	3.09	2.81		2
$[ClBr_2Au(Ph_2PCH_2PPh_2)AuClBr_2]$	4.01	2.68		2
$[Cl_3Au(Ph_2PCMe_2PPh_2)AuCl_3]$	2.41	2.00		2
$[Cl_3Au(Ph_2PNMePPh_2)AuCl_3]$	2.95	2.45		3
$[(Br_2AuCH_2PEt_2CH_2)_2]$	3.22	5.52		12

[a] This work. [b] Data for gold(III) atom only. [c] thfbd = *trans*-$C(CF_3)$=$C(CF_3)$. [d] J. A. Jarvis, A. Johnson, and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, 1973, 373. [e] chfbd = *cis*-$C(CF_3)$=$C(CF_3)$. [f] R. V. Parish and J. D. Rush, quoted in ref. 13.

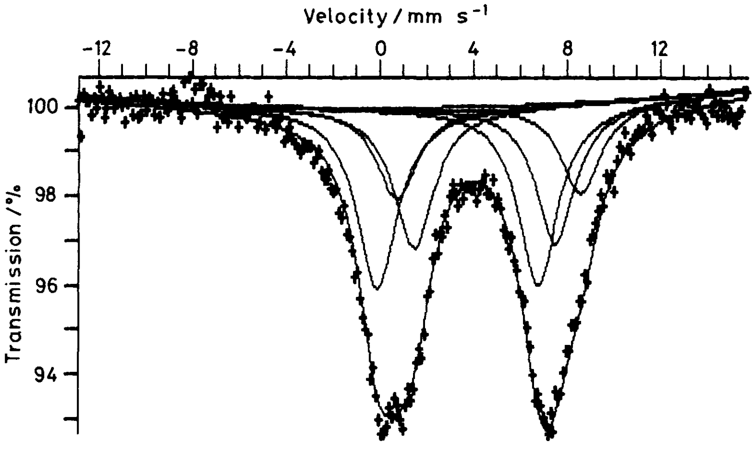

Figure 1. ^{197}Au Mössbauer spectrum of $[Au_2(dppa)_2Br_2][ClO_4]_2$

between ln *f* and the reciprocal molar mass.[18] For a given molar mass, *f* is substantially larger for gold(III) than for gold(I). In the present case, both gold atoms are part of the same molecule, but the effective recoiling mass would be greater for the $(dppa)Au^{III}Cl(C_6F_5)_2$ unit than for $(dppa)Au^{I}Cl$. Estimates from the data available[14] suggest that an intensity ratio of 2:1 is not unreasonable.

The gold(II + II) complexes have parameters which are distinct from those of gold(I) and gold(III), but are close to those of related compounds. The complexes $[Au_2(dppa)_2X_2][ClO_4]_2$ (X = Cl or Br) had clearly undergone some change before the Mössbauer spectra could be recorded, and three species were detected in each sample. One set of signals were consistent with the expected gold(II + II) formulation with structure (**10**). The other two correspond to gold(I) and gold(III) but are not consistent with structure (**8**), which is the expected disproportionation product.

The parameters for gold(II) compounds now available are

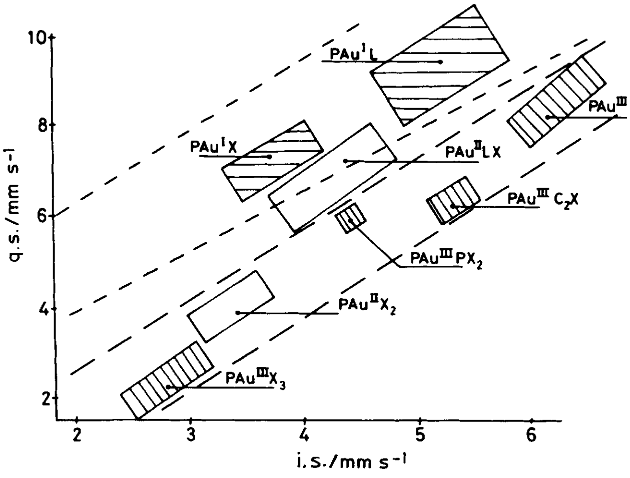

Figure 2. I.s.–q.s. correlation diagram showing the major areas corresponding to gold(I), gold(II), and gold(III) complexes with various co-ordinations (L = C- or P-donor ligand, C = C-donor ligand, P = P-donor ligand, X = Cl or Br). The upper and lower bands marked with dotted lines indicate the regions defined by previous data for gold(I) and gold(III) complexes, respectively

best discussed in terms of the i.s.–q.s. correlation diagram (Figure 2), in relation to those for corresponding gold(I) and gold(III) complexes (*i.e.* those which contain one fewer or one more halide ligand, but the same number of 'soft' ligands). Two types of complex have now been examined. Those previously reported, with structures of the type (**9**; Y = CH_2, CMe_2, or NMe)[2,3] and $PAu(Au)X_2$ co-ordination, have parameters which lie within the range normally associated with gold(III) complexes, but have slightly greater i.s. and q.s., *i.e.* are displaced towards the corresponding gold(I) data. For the new compounds, of structures (**9**) and (**10**) (Y = NH), with PAu(Au)LX co-ordination (L = P- or C-donor), the distinction appears to be slightly greater, although there are only two corresponding gold(III) points for comparison. The new gold(II) data certainly lie outside the region presently identified for gold(III), in the direction of the corresponding gold(I) complexes. For both sets of compounds, an increase in formal oxidation state is correlated with a small increase in i.s. and a substantial increase in q.s. The replacement of a poorly donating halide ligand by a 'softer' phosphine or organic group results in an increase in both parameters, in the same way, and for the same reasons as for gold(I) and gold(III).

To understand the electronic factors involved requires an interpretation of the correlation diagram. For both gold(I) and gold(III), increasing donation from the ligands simultaneously increases the i.s. and the q.s. Increased donation augments the 6*s* electron density on the gold atom, and hence raises the i.s. The i.s. for gold(III) would be expected to be greater than for gold(I) because of the reduced shielding of the *d* shell (d^8 *vs.* d^{10}), but lower due to the increase in co-ordination number. For the same ligands, the first effect seems to be slightly the greater. The q.s. also rises with increasing donation in both cases because, other things being equal, two ligands on the *z* axis [gold(I)] would make a similar contribution to the electric-field gradient (e.f.g. = V_{zz}) to that from four ligands on the *x* and *y* axes [gold(III)]. However, in the latter case, there is an opposing contribution from the full d_{z^2} orbital, so that the q.s. for a gold(III) complex is less than that for the corresponding gold(I) complex. The rate of change in q.s. with change of ligand is different for the two oxidation states because of the difference in hybridisation, *sp vs. dsp*^{2}; the increased *p*–*d* participation for gold(III) results in more rapid change of the e.f.g. with bond population. For gold(III), the ligand contribution to the e.f.g. is about equal to that of the d_{z^2} orbital when four halide ions are co-ordinated.

In gold(II + II) complexes the co-ordination of the gold atoms resembles that of gold(III) systems, except that one 'ligand' is the other gold atom. There is formally an additional electron in the $d_{x^2-y^2}$ orbital, which would substantially raise the q.s. above the value for the corresponding gold(III) complex. This electron would also be expected to exert a shielding effect on the electron density at the nucleus, and thus to decrease the i.s. The fact that the i.s. rises slightly indicates that there is also a contribution to the 6*s* population from the gold–gold bond, *i.e.* the second gold atom acts as a 'soft' ligand. Support for this idea comes from the observation that the q.s. values of gold(II) complexes with two 'soft' ligands [PAu(Au)LX] are comparable with those of gold(III) complexes with three 'soft' ligands ($PAuL_2X$). The full shielding effect of the ninth *d* electron is now seen in the diminution of the i.s.

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