Gold-197 Mössbauer Spectra and the Bonding of Some Gold–Gold and Gold–Platinum Clusters

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The ^{197}Au Mössbauer parameters of the $AuPt_3$, Au_2Pt_2, and Au_2Pt_3 clusters $[AuPt_3(\mu\text{-}CO)_3L_4]^+$, $[Au_2Pt_2L_4(CNR)_4]^{2+}$, $[AuPt_3(\mu\text{-}SO_2)_2(\mu\text{-}Cl)L_4]$, and $[Au_2Pt_3(\mu\text{-}SO_2)_2(\mu\text{-}Cl)L_4]$ [L = $P(C_6H_{11})_3$ or $P(C_6H_4F\text{-}p)_3$, R = xylyl] are consistent with the bonding schemes previously proposed, showing a diminution with increasing delocalisation of the bonding electrons and increase in the metal–metal bond lengths. Separate signals are resolved for the non-equivalent gold atoms in $[Au_6\{P(C_6H_{11})Ph_2\}_6]^{2+}$, the parameters and intensities of which correlate with the expected electron densities and observed connectivities of the gold atoms. The centred-crown cluster $[Au_9L_8]^{3+}$ [L = $P(C_6H_4OMe\text{-}p)_3$] gives slightly greater parameters than its icosahedral-fragment analogues, consistently with the observed shortening in Au–Au contacts. No separate signal is resolved for the central gold atom.

Gold forms a variety of metal–metal bonded compounds, both homonuclear and heteronuclear, in which the bonding ranges from simple covalent, two-centre two-electron bonds to highly delocalised systems encompassing large clusters. We have recently demonstrated that Mössbauer spectroscopy is a useful means of distinguishing these possibilities for small molecules containing gold and iron.[1] It has also been shown that, in both homonuclear and heteronuclear clusters, the Mössbauer parameters correlate with increasing electron delocalisation, bond lengths, and connectivities.[2,3]

Further, we have shown that the Mössbauer method is capable of distinguishing distinct signals from gold atoms occupying non-equivalent positions in gold–ruthenium clusters, even though they are bound to the same external ligand.[2,4] For homonuclear gold clusters, such an observation has been reported only once (ref. 5, but see footnote in ref. 2). Since cluster compounds can normally be characterised only by *X*-ray crystallography, it would be useful to establish the types of cluster for which a 'sporting' technique can give useful structural information.

We now present ^{197}Au Mössbauer data for homonuclear clusters involving Au_6 and Au_9 units and heteronuclear clusters in which gold is bound to various Pt_3 units.

Experimental

Mössbauer spectra were recorded as described previously,[6] with both source (Pt/Au) and sample (*ca.* 20 mg Au cm^{-2}) immersed in liquid helium. Isomer shifts are quoted relative to metallic gold at 4.2 K. Spectra were fitted with unconstrained Lorentzian functions except for that of $[Au_6\{P(C_6H_{11})Ph_2\}_6][BF_4]_2$, where the severe overlapping of two doublets made it necessary to constrain the lines in pairs (equal widths and intensities).

Syntheses.—The compounds (**1**) and (**3**)—(**7**) were prepared according to the published procedures.[7–10]

$[Pt_3Au(\mu\text{-}SO_2)_2(\mu\text{-}Cl)\{P(C_6H_{11})_3\}_4]$, (**2**). The compound $[Pt_3(\mu\text{-}SO_2)_3\{P(C_6H_{11})_3\}_3]$[11] (0.24 g, 0.15 mmol) was dissolved in benzene (30 cm^3) and $[AuCl\{P(C_6H_{11})_3\}]$ (0.076 g, 0.015 mmol) was added with stirring. The solution turned orange over 20 min, after which the solvent was removed under reduced pressure, giving bright yellow crystals. Benzene (30 cm^3) was added, the mixture was warmed, allowed to cool, and the product was filtered off. Yield, 0.24 g, 77% (Found: C, 41.8; H, 6.3. $C_{72}H_{132}AuClO_4P_4Pt_3S_2$ requires C, 41.8; H, 6.4%); $\nu(SO_2)$ 1 174 and 1 046 cm^{-1}.

Results and Discussion

$AuPt_3$ *Clusters.*—Compounds (**1**)—(**3**) involve a single R_3PAu unit bonded to $Pt_3(PR_3)_3$ triangles in which the edge-bridging groups are either three CO molecules or two SO_2 molecules plus a chloride ion. The $AuPt_3$ unit forms a tetrahedral cluster.[6,12] Compounds (**2**) and (**3**) differ only in the identity of the phosphine bound to the gold atom. Three major observations can be made about the data for these compounds (see Table 1). (*i*) The parameters fall within the band of values established for two-co-ordinate, linearly hybridised gold(I) complexes of the type $[AuL(PR_3)]$.[13] (*ii*) The parameters lie at the lower end of this range. (*iii*) It is evident that the Mössbauer parameters for compounds (**1**) and (**2**) are essentially the same, suggesting that changes in the bridging groups on the Pt_3 unit have little effect on the bonding of the gold atom in the cluster.

The difference in parameters between compounds (**2**) and (**3**) are consistent with the normal trend that aryl phosphines are significantly poorer donors to gold than aliphatic phosphines[13] (*cf.* $[AuCl\{P(C_6H_{11})_3\}]$, isomer shift (i.s.) 4.43, quadrupole splitting (q.s.) 7.59 mm s^{-1}; $[AuCl(PPh_3)]$, i.s. 4.08, q.s. 7.43 mm s^{-1}); in this case, the effect is accentuated by the *p*-fluoro substituent.

Points (*i*) and (*ii*) emphasise that the gold is contributing only a single valence orbital (*sp* hybrid) to the cluster bonding. This confirms the isolobal analogy usually made in the treatment of gold cluster compounds.[14] If the gold were employing four valence orbitals in binding the phosphine and three platinum atoms, both parameters would be expected to be considerably smaller.[13] The bonding in triangular clusters is well understood.[15] In the case of systems in which the three metal atoms each have one inward-pointing orbital to contribute to the cluster bonding, these orbitals combine to form a single bonding orbital (a_1') and a degenerate pair of antibonding orbitals (e'). In the case of a $Pt_3(\mu\text{-}CO)_3L_3$ cluster, the a_1' orbital contains two electrons, and is the highest occupied molecular orbital (h.o.m.o.) [Figure 1(*a*)]. In the $AuPt_3$ cluster $[Pt_3Au(\mu\text{-}CO)_3\{P(C_6H_{11})_3\}_4]PF_6$ (**1**) the gold atom of the LAu^+ capping unit is linearly *sp* hybridised. One hybrid accepts a pair of

Table 1. Data (mm s^{-1}) for $AuPt_3$ clusters

	Compound	I.s.[a,b]	Q.s.[b]	Linewidths[c]
(**1**)	$[Pt_3Au(\mu\text{-}CO)_3\{P(C_6H_{11})_3\}_4]PF_6$	3.83	6.58	1.90, 2.04
(**2**)	$[Pt_3Au(\mu\text{-}SO_2)_2(\mu\text{-}Cl)\{P(C_6H_{11})_3\}_4]$	3.69	6.67	2.24, 2.00
(**3**)	$[Pt_3Au(\mu\text{-}SO_2)_2(\mu\text{-}Cl)\{P(C_6H_{11})_3\}_3\{P(C_6H_4F\text{-}p)_3\}]$	3.27	6.30	1.89, 2.18
(**4**)	$[Pt_2Au_2(\mu\text{-}SO_2)_2(\mu\text{-}Cl)\{P(C_6H_{11})_3\}_3\{P(C_6H_4F\text{-}p)_3\}_2][PF_6]$	3.30	5.75	1.95, 2.14
(**5**)	$[Pt_2Au_2(PPh_3)_4(CNC_6H_3Me_2)_4][PF_6]_2$	3.13	6.88	2.05, 1.80
(**6**)	$[Au_6\{P(C_6H_{11})Ph_2\}_6][BF_4]_2$[d]	3.58[c]	8.39[c]	1.87
		3.23[c]	6.20[c]	2.08
(**7**)	$[Au_9L_8][NO_3]_3$[e]	3.52	6.95	2.25, 2.06

[a] Relative to metallic gold. [b] ± 0.03 mm s^{-1}. [c] ± 0.05 mm s^{-1}. [d] The figures given are for the nested fit. The overlapped fit gives i.s. 2.98 and 4.50, q.s. 6.90 and 7.67, and linewidths 2.32 and 1.62 mm s^{-1} respectively. [e] L = $P(C_6H_4OMe\text{-}p)_3$.

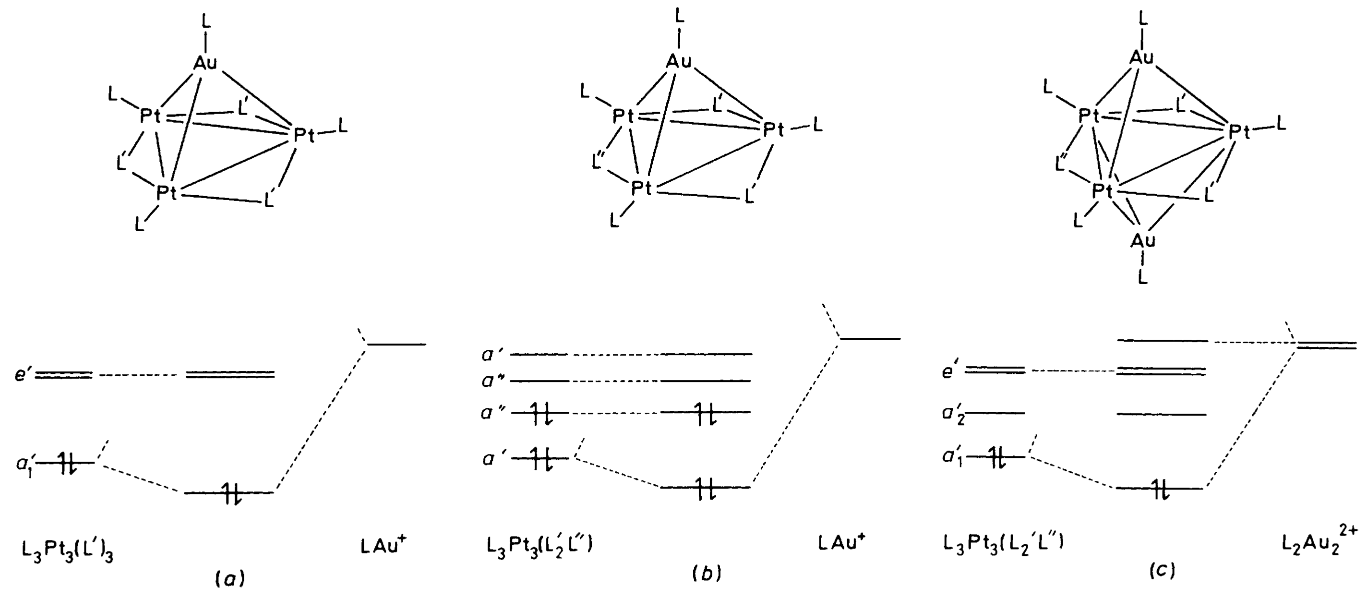

Figure 1. Principal molecular orbitals for the metal skeletons of (*a*) $[AuPt_3(\mu\text{-}L')_3L_4]^+$ (L = PR_3, L′ = CO), (*b*) $[AuPt_3(\mu\text{-}L')_2(\mu\text{-}L'')L_4]$ (L = PR_3, L′ = SO_2, L″ = Cl), (*c*) $[Au_2Pt_3(\mu\text{-}L')_2(\mu\text{-}L'')L_5]^+$(L = PR_3, L′ = SO_2, L″ = Cl)

electrons from the phosphine ligand, the other overlaps with the a_1' orbital of the Pt_3 unit, forming a four-centre two-electron bond linking the four metal atoms. The increase in delocalisation of the pair of electrons in the a_1' orbital weakens the Pt–Pt bonding, as is evidenced by an increase in the average Pt–Pt distances of 0.041 Å.[12,16] The low population of the (Au)*sp* orbital is indicated by the low values of the Mössbauer parameters, which are smaller than those of the complexes $[AuCl(PR_3)]$ mentioned above.

Similar trends are found for $[Pt_3(\mu\text{-}SO_2)_2(\mu\text{-}Cl)\{P(C_6H_{11})_3\}_3]$ and its gold adduct, $[Pt_3Au(\mu\text{-}SO_2)_2(\mu\text{-}Cl)\{P(C_6H_{11})_3\}_4]$ (**2**). In these cases, the bond distances are not known for the parent cluster, but the computed reduced Pt–Pt overlap populations change from 0.142 to 0.113.[15]

The lack of sensitivity of the Mössbauer parameters to change in the bridging ligands on the platinum triangle [compounds (**1**) and (**2**)] is at first sight surprising, especially when it is remembered that the $Pt_3(\mu\text{-}SO_2)_2(\mu\text{-}Cl)^-$ unit contains two extra electrons. However, these electrons are housed in an *a*″ orbital which is mildly antibonding with respect to the platinum triangle [Figure 1(*b*)], but has the wrong pseudo-symmetry to interact with the gold.[15] Thus, the Pt–Pt bonding is weakened slightly [increase of 0.168 Å in bond length, between (**1**) and (**3**)], but the Au–Pt interaction is virtually unaffected (0.029 Å decrease in bond length, which may be partly due to rehybridisation of the gold resulting from the change in phosphine ligand).

When a second $Au(PR_3)$ unit is added to the cluster, compound (**4**), its *sp* hybrid orbital interacts with the a_1' orbital, which thus becomes a five-centre orbital [Figure 1(*c*)]. This pair of electrons is now even further delocalised, and there is a consequent increase in both the Pt–Pt and Au–Pt bond lengths by 0.056 and 0.022 Å respectively. The greater sensitivity of the Pt–Pt interaction is confirmed by the reduced overlap populations, which decrease from 0.113 to 0.087 (23%) while the Au–Pt populations change only from 0.093 to 0.088 (5.4%). There is a corresponding decrease in q.s. for the gold atom. The i.s. is unchanged. The greater sensitivity of the q.s. is also analogous to that for other R_3PAuX systems, and derives from the fact that the q.s. responds to change in the $(Au)6p_z$ population. Since the phosphine ligand is relatively soft, the (Au)*sp* hybrid orbital used in bonding it may be expected to have relatively high *s* character; the remaining hybrid, used in bonding to the platinum atoms, will have correspondingly high *p* character.

The Pt_2Au_2 *System.*—The compound $[Pt_2Au_2(PPh_3)_4(CNC_6H_3Me_2\text{-}2,6)_4][PF_6]_2$ (**5**) has a butterfly structure with the Au_2 unit forming the body, and two perpendicular $Pt(PPh_3)(CNC_6H_3Me_2\text{-}2,6)$ units the wings.[17] There is thus no

Table 2. Average bond distances (Å)

Compound	*d*(Au–Pt)	*d*(Pt–Pt)	*d*(Au–Au)	Ref.
(1)	2.758	2.696		11
(3)	2.729	2.864		5
(4)	2.785	2.886		
(5)	2.884		2.590	16
(6)			2.753, 2.767	17

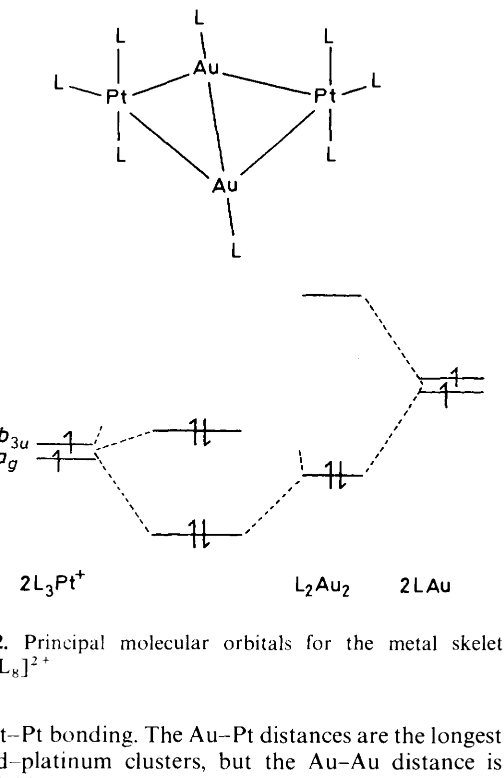

Figure 2. Principal molecular orbitals for the metal skeleton of $[Au_2Pt_2L_8]^{2+}$

direct Pt–Pt bonding. The Au–Pt distances are the longest of all the gold–platinum clusters, but the Au–Au distance is very short (Table 2). The crystal structure shows that the gold atoms are not equivalent, there being two sets of Au–Pt distances (average values, 2.714 and 2.974 Å). There is, however, no indication of such non-equivalence in the Mössbauer spectrum.

The bonding in this cluster is best described in terms of the interaction of an L_2Au_2 unit with two L_3Pt units (Figure 2).[15] The latter are isolobal with LAu, having one singly occupied valence orbital. These two platinum orbitals overlap with the bonding m.o. of the Au_2 unit (σ_g combination of the two inward-pointing *sp* hybrids), forming a four-centre two-electron bond which unites the cluster. A higher-energy occupied molecular orbital (b_{3u}) is essentially non-bonding. Thus, the electron density in the hybrid orbitals of the gold atoms is again low, explaining the small values of the Mössbauer parameters.

In line with the large bond lengths, the i.s. is the lowest of all the gold–platinum clusters. There may also be a negative contribution to the i.s. from the stabilisation of the (Au)*d* shell,[15] which would increase the shielding of the nucleus from *s*-electron density. The q.s., however, is the largest of the series. This is presumably due to the low symmetry of the gold site. In the tetrahedral clusters the gold occupies a site of essentially trigonal symmetry, whereas the local symmetry of the gold atoms in the butterfly cluster is C_s: the asymmetry parameters will thus be non-zero and will augment the q.s.

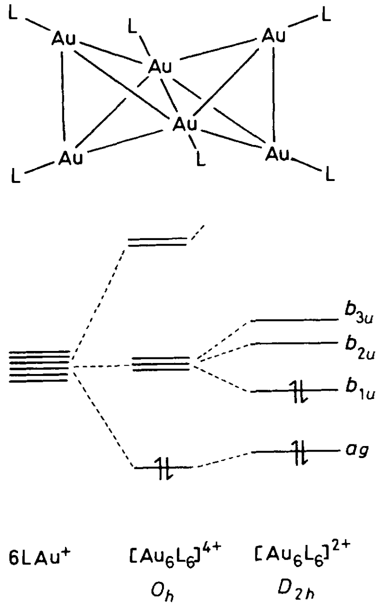

Figure 3. Principal molecular orbitals for the metal skeleton of $[Au_6L_6]^{2+}$

The Au_6 *Cluster*.—The compound $[Au_6\{P(C_6H_{11})Ph_2\}_6][BF_4]_2$ (6) is analogous to $[Au_6(PPh_3)_6][NO_3]_2$, which is known to have a structure consisting of two Au_4 tetrahedra fused at one Au_2 edge.[10,18] In this molecule there are two distinctly different types of gold atom: the two central atoms form a short link to each other [2.651(2) Å] and are also bonded to the four peripheral atoms; these latter form relatively short links within the pairs [2.666(2) Å], and form longer bonds to the central atoms [2.796(2) Å]. The six atoms are bonded by four electrons in two molecular orbitals (Figure 3). The lower-energy orbital (a_g) is essentially localised between the two central atoms. The upper orbital (b_{1u}) contributes one six-centre two-electron bond, but the electron density is not uniformly distributed. This orbital is strongly bonding along the two outer edges and the central shared edge of the tetrahedra, and more weakly bonding (π bonding) along the side edges. Overall, therefore, the central gold atoms carry the higher electron density.

The Mössbauer spectrum, although somewhat noisy (Figure 4), clearly shows the presence of more than one doublet, and is similar to those of the gold–ruthenium clusters reported earlier.[3,4] The higher-velocity absorption is broader and less intense than that at lower velocity. This is the usual pattern,[19] and results from the greater sensitivity of the q.s. than i.s. to changes in bonding. For series of complexes of the type $[AuX(PR_3)]$, the q.s. increases approximately twice as fast as the i.s.; thus, the lower-velocity lines superpose much more closely than those at high velocity. Two fittings are possible, with the two doublets either nested or overlapped, and their parameters differ by more than the estimated uncertainties. For series of related compounds, nested fits are expected, but this might not apply when, as here, the gold atoms have different environments. In this case, further guidance is available from the ratio of the areas of the two components. The two types of gold atom are present in 2:1 ratio, and the spectra show a corresponding difference in intensity. For the nested fit the area ratio is 1.4:1, while for the overlapped fit it is 2.3:1.* It has previously been shown that the intensities are related to the

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* A referee has pointed out that the constraints employed may bias the area ratios. Unconstrained fits give rather small widths for some of the lines but do not significantly affect either the parameters or the area ratios.

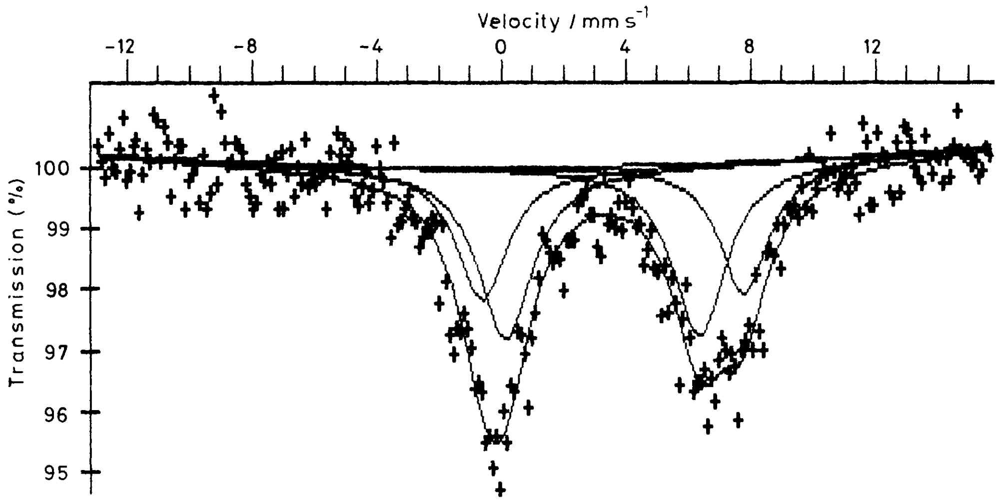

Figure 4. ^{197}Au Mössbauer spectrum of compound (**6**)

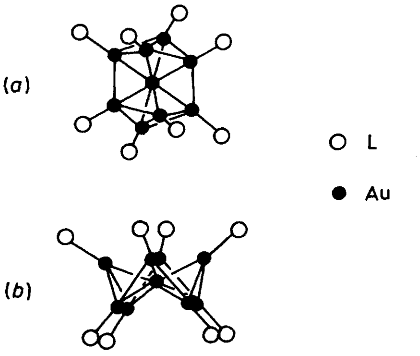

Figure 5. The two isomers of $[Au_9L_8]^{3+}$ (**7**). The form measured here is (*b*)

effective masses of the gold atoms plus their immediate neighbours.[2] In the present case, the recoiling units are PAu_4 (terminal; mass, M 622) and PAu_6 (central; M 819): the central atoms are therefore expected to have the larger recoil-free fraction, and the calculated area ratio is 1.6:1. The nested fit is therefore preferred.

On this basis, the central gold atoms have the larger Mössbauer parameters, which is consistent with the higher electron density associated with the inward-pointing hybrid orbitals on these atoms. There is probably also a further contribution to the q.s. from the lower symmetry of these atoms (C_{2v}) than the outer atoms (effectively C_{3v}).

The Au_9 *Cluster*.—The majority of Au_9 clusters have structures based on a metal-centred icosahedron. However, it is known that such clusters are stereochemically non-rigid in solution, and it has recently been found that the centred-crown geometry is also possible in the solid state.[20] Indeed, in one case, both forms have been isolated (Figure 5).[21] Mössbauer spectroscopic data have been reported for several of the icosahedral-fragment clusters,[22] and it was of interest to determine whether the parameters are sensitive to change in the skeletal arrangement.

The Mössbauer spectra of the icosahedral-fragment clusters show strong signals with i.s. 3.1 mm s^{-1} and q.s. 6.6—6.8 mm s^{-1}. These ranges are very close to those of compound (**7**) (Table 1), with the latter possibly being marginally the greater. This trend is in agreement with the slightly smaller average Au–Au bond lengths: the radial and peripheral Au–Au distances are 2.668 and 2.823 Å for the centred crown [compound (**7**)], and 2.712 and 2.825 Å for its isomer.[21]

A more significant observation is perhaps the lack of an observable signal for the central gold atom. The compound $[Au_9(PPh_3)_8][PF_6]_3$ behaves similarly, but when the anion is a halide or pseudohalide a single line is observed. In view of its high connectivity and large effective mass, the central atom would be expected to show more than one ninth of the total intensity. The lack of an observable signal has been attributed to the relatively low symmetry of the central site;[23] the central gold atom is thus expected to show quadruple splitting similar to that of the peripheral atoms.

Conclusions

The ^{197}Au Mössbauer data for gold-containing clusters reported here are consistent with the known structures and with previous descriptions of bonding. In particular, signals for non-equivalent gold atoms in $[Au_6\{P(C_6H_{11})Ph_2\}_6][BF_4]_2$ have been resolved; as with heteronuclear clusters, the integrated intensities of the two signals are not directly proportional to the numbers of gold atoms involved, but also reflect their effective masses.

The Mössbauer parameters for the clusters, both those reported here and previously, lie in the same region of i.s.–q.s. space as those for simple two-co-ordinate gold (I) compounds of the type $[AuX(PR_3)]$. The data therefore do not directly reflect the apparent co-ordination number of the gold atoms. This observation gives direct support to the isolobal analogy and suggests that, for cluster compounds, it would be better to assign an 'orbital number' than a co-ordination number; that is, the gold atom is employing only two hybrid orbitals to bind the external ligand and the other atoms of the cluster. The gold–platinum clusters show that, as with homonuclear clusters, the Mössbauer parameters become smaller as the extent of delocalisation of the cluster bonding electrons increases.

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