Detection of Non-equivalent Gold Sites in Mixed-metal Cluster Compounds by Mössbauer Spectroscopy

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The first ^{197}Au Mössbauer data for mixed-metal cluster compounds are reported; structurally non-equivalent gold atoms bearing the same exo-ligands can be distinguished in gold–ruthenium clusters.

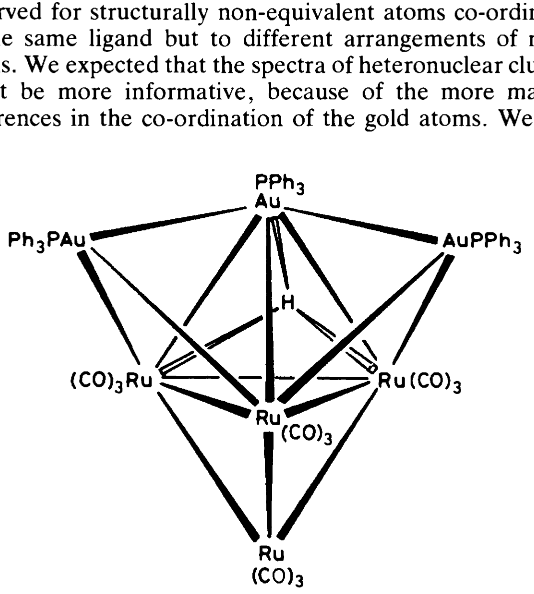
Mössbauer spectroscopy has proved to be of great value in the characterisation of simple compounds and complexes of gold.[1] However, attempts to use the technique to investigate the skeletal geometries of homonuclear cluster compounds of

Table 1. ^{197}Au Mössbauer data for clusters (**1**), (**2**), and (**3**) (4.2 K).

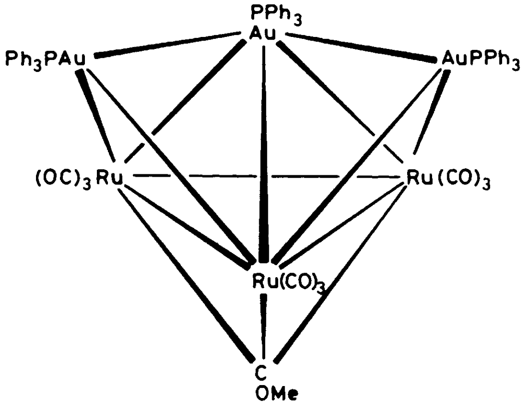
		I.S.(Au)[a]/ mm s^{-1}	Q.S.[b]/ mm s^{-1}	Line width[c]/ mm s^{-1}	Area ratio[d] a : b	Co-ordination
(**1**)	a	3.0	7.4	2.0	1.3	$AuRu_2P$
	b	2.0	4.9			Au_2Ru_3HP
(**2**)	a	2.7	7.0	2.5	1.6	$AuRu_2P$
	b	2.4	5.2			Au_2Ru_3P
(**3**)	a	3.0	7.5	2.0	1.1	$AuRu_2P$
	b	2.3	5.4			$AuRu_3HP$

[a] Isomer shift, ±0.1 mm s^{-1}. [b] Quadrupole splitting, ±0.2 mm s^{-1}. [c] ±0.2 mm s^{-1}. [d] ±0.3.

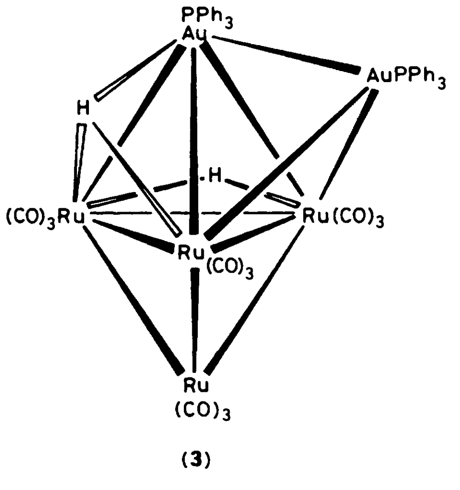
gold have proved somewhat disappointing.[2] Although it is easy to distinguish the signals for peripheral atoms bearing different exo-ligands (*e.g.* halides and tertiary phosphines), there is only one report[3] of resolved sub-spectra being observed for structurally non-equivalent atoms co-ordinated to the same ligand but to different arrangements of metal atoms. We expected that the spectra of heteronuclear clusters might be more informative, because of the more marked differences in the co-ordination of the gold atoms. We now report the first ^{197}Au Mössbauer spectra for such clusters, and we demonstrate that the technique can resolve signals due to structurally non-equivalent Au(PPh_3) units within one cluster. Such information is potentially extremely valuable, since many such clusters undergo dynamic behaviour in solution which involves gold atom site-exchange.[4—7] It is, therefore, often impossible to obtain n.m.r. spectra corresponding to the ground state structures[5—7] unless measurements can be made directly on solid samples.[8]



(1)



(2)



(3)

In the clusters $[Au_3Ru_4(\mu_3\text{-}H)(CO)_{12}(PPh_3)_3]$ (**1**),[4] $[Au_3Ru_3(\mu_3\text{-}COMe)(CO)_9(PPh_3)_3]$ (**2**),[5] and $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)(CO)_{12}(PPh_3)_2]$ (**3**),[6] all of the gold atoms carry a single PPh_3 ligand, but each molecule contains two distinct gold sites. In clusters (**1**) and (**2**), there are two gold atoms which have another gold atom and two ruthenium atoms as neighbours, Au(Au'Ru_2); in (**3**) there is one such gold atom. The second gold site is different in each case: Au(Au'$_2Ru_3$H) in (**1**), Au(Au'$_2Ru_3$) in (**2**), and Au(Au'Ru_3H) in (**3**). The Mössbauer spectra† all show considerable broadening of the higher-velocity absorption, with corresponding diminution in intensity (see Figure 1). For (**1**), it is evident even without computer fitting that this absorption contains two components, indicating the presence of two doublets. The general systematics of ^{197}Au Mössbauer parameters for gold(I) compounds and gold clusters result in much closer overlap of the lower-velocity lines,[1,9] and also imply that the doublets should be nested rather than overlapped; we have used this as a guide to assignment, and have fitted two nested doublets to each spectrum. The derived data (see Table 1) show that the wider doublet has similar parameters in all three cases: isomer shift *ca.* 2.9 mm s^{-1}, quadrupole splitting *ca.* 7.3 mm s^{-1}. Since for (**1**) and (**2**) this doublet is also the more intense, it is assigned to the Au(Au'Ru_2) unit. These parameters are similar to those for other clusters containing the same unit.[10] The inner doublet therefore corresponds in each case to the gold atom with the larger number of neighbours. (The intensity ratios do not correspond exactly to the ratio of numbers of gold atoms. This is not unusual for cluster compounds, and is partly due to the difficulties in obtaining unique fits to heavily overlapped spectra. However, it is also probable that the different gold sites have different recoil-free fractions.[11])

The new data fall in the range previously observed for homonuclear clusters.[2] In such systems there is a very small trend to decreasing isomer shift with increasing size of the cluster, *i.e.* with increasing numbers of metal–metal contacts.[1,2] This effect is considerably magnified in the Au–Ru clusters, presumably because of the greater electronegativity of ruthenium than gold; evidence has been presented to show that the presence of CO ligands considerably increases the effective electronegativity (Lewis acidity) of metal atoms.[12]

It is clear that ^{197}Au Mössbauer spectroscopy can distinguish between geometrically different Au(PPh_3) sites within a single cluster. Indeed, our results suggest that it may well be possible to interpret the spectra of new clusters without a detailed prior knowledge of the molecular structure, which has so far not been possible.

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† Mössbauer spectra were obtained in transmission mode with source (irradiated enriched ^{196}Pt) and sample [*ca.* 25 mg(Au) cm^{-2}] immersed in liquid helium, using a high-purity germanium detector. Isomer shifts are quoted relative to metallic gold at 4.2 K. Because of the heavy overlapping of the two doublets, it was necessary to apply constraints during the fitting: the four absorptions lines were constrained to have equal widths, and the two lines of each doublet to have equal intensities. The uncertainties, especially those in the relative intensities, are correspondingly large.

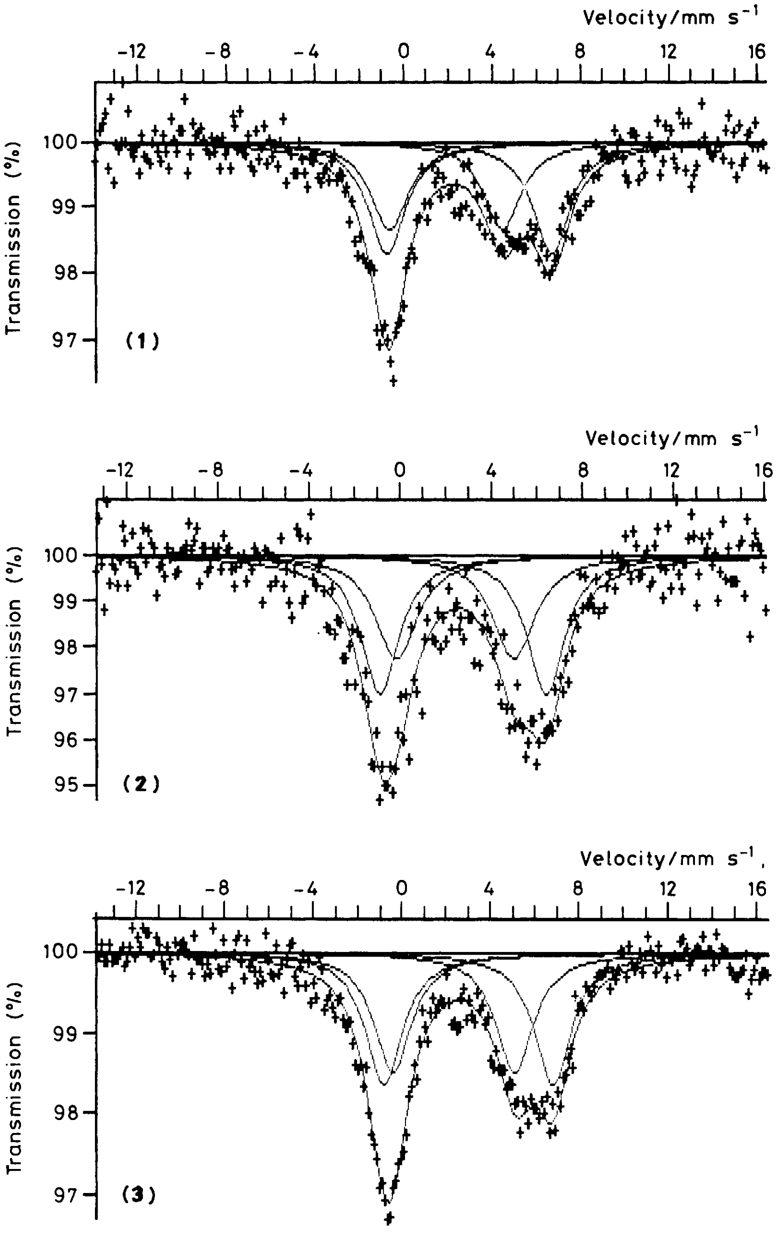

Figure 1. ^{197}Au Mössbauer spectra of compounds (**1**), (**2**), and (**3**).

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