Studies of Gold Cluster Compounds using High-resolution ^{31}P Solid-state Nuclear Magnetic Resonance Spectroscopy *

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High-resolution ^{31}P n.m.r. spectra of a series of crystalline gold phosphine cluster compounds have been obtained using magic angle sample spinning. The spectra are interpreted on the basis of the known crystal structures, and are compared with corresponding spectra of the compounds in solution. With one exception, the clusters appear to be stereochemically rigid in the crystals at room temperature, although most are fluxional in solution, some even at low temperatures. In many cases separate resonances can be resolved in the solid-state spectra from the distinct phosphine environments of the cluster framework. A combination of solid-state and solution n.m.r. spectroscopy is likely to be extremely valuable in the characterisation of both the structure and dynamics of phosphine-containing cluster compounds.

A wide variety of metal cluster compounds has now been prepared and characterised.[1] These compounds contain metal–metal bonds and have a sufficient number of atoms to define a three-dimensional polyhedral core. Molecular clusters of gold are stabilised by tertiary phosphines (PR_3) and halide ligands (X).[2] Low-nuclearity clusters are defined by the formula $[Au_x(PR_3)_{x+y}]^{n+}$, where $y = 0$—2, whilst the higher-nuclearity clusters have an additional central gold atom and can be written as $[Au_{x+1}(PR_3)_{x-y}X_y]^{n+}$.

Phosphorus-31 n.m.r. studies have shown that the majority of gold clusters are stereochemically non-rigid in solution, often giving averaged spectra even at low temperatures.[3] The fluxional behaviour is thought to result from facile skeletal rearrangement, and is common to all types of clusters with the exception of the icosahedral compounds. Recently preliminary accounts of the high-resolution ^{31}P n.m.r. spectra of gold clusters in the solid state have been reported.[4,5] The results indicated that there were differences between spectra in solution and in the solid state which could be related to fluxional behaviour. Differences in the fluxional properties of molecules in the solid state and in solution have been observed for metal carbonyl cluster compounds.[6,7]

In this paper we report a systematic study of the high-resolution solid-state ^{31}P n.m.r. spectra of a series of gold clusters, all with known crystal structures. Apart from the intrinsic interest in the difference in dynamic properties in the solution and solid states, a clear understanding of the factors affecting the solid-state spectra of the compounds is important if the n.m.r. technique is to be used for structural studies. If fluxional processes occurring in solution are frozen out in the solid the solid-state ^{31}P n.m.r. spectra will reveal more directly than those of the solutions the unique phosphine environments and hence the structure of the cluster.

Experimental

The following gold clusters were prepared using methods described previously: $[Au_6\{P(C_6H_4Me\text{-}o)Ph_2\}_6][NO_3]_2$;[8] $[Au_8\{P(C_6H_4OMe\text{-}p)_3\}_8][NO_3]_2$;[8] $[Au_9\{P(C_6H_4OMe\text{-}p)_3\}_8]X_3$ ($X = NO_3$ or BF_4);[9,10] $[Au_{13}Br_4(PMePh_2)_8]Br$;[8] and $[Au_{13}(PMe_2Ph)_{10}Cl_2][PF_6]_3$.[11] Crystal structures and solution n.m.r. spectra have been reported previously. Solid-state n.m.r. spectra were obtained on a Bruker CXP200 spectrometer operating at 80.96 MHz for ^{31}P and 200.13 MHz for ^{1}H. Magic angle sample spinning[12] was carried out using a Delrin Andrews-type rotor with typical spinning speeds of *ca.* 4 kHz. Cross-polarisation was used for most experiments in order to enhance the sensitivity;[13] the Hartman–Hahn condition was met with a B_1 field of 10 G for ^{1}H and 24.7 G for ^{31}P. The use of cross-polarisation can lead to deceptive relative intensities, consequently the observed intensities were compared in ^{31}P n.m.r. spectra obtained using different cross-polarisation times (between 0.5 and 10 ms) and by direct observation of the ^{31}P signal without enhancement. No significant differences were observed in the relative intensities upon altering the contact time. From these experiments the optimum contact time for cross-polarisation was found to be 1.5 ms. Typically, several thousand transients were accumulated using a recycle delay of 2 s with 50—100 mg of sample at 20 °C. The magic angle setting of 54° 44′ was optimised by minimising the linewidth of the carbonyl resonance in the ^{13}C spectrum of glycine. Considerable care was taken in setting the magic angle because splitting of resonances was observed when the angle was incorrectly adjusted.

Results

The ^{31}P spectrum of each of the gold cluster compounds in the solid state consists of a number of peaks with chemical shifts between 37 and 71 p.p.m., each of which has a series of sidebands spaced at the spinning frequency. For the spinning speeds used in this work the sideband intensities are small, and represent less than 25% of the total signal intensity in each case. These could be neglected in the estimation of the relative intensities of the different peaks because the chemical shift anisotropies as revealed by the relative intensities of the spinning sidebands were found to be similar for the different phosphines in a given molecule.

The linewidths of the resonances in the solid-state spectra were found to be typically 300 Hz, much greater than those of the corresponding solution spectra, which were generally <5 Hz. At least part of the linewidth in the solid state can be attributed to dipolar broadening due to the ^{197}Au nuclei, which is absent in solution. This is not removed by magic angle spinning because the quadrupole interaction of the gold is comparable in magnitude with the nuclear Zeeman interaction.[14] Despite the broad lines, many of the peaks are well resolved, and the number of distinct resonances observed in the solid state is at least as great, and generally greater, than that observed in the corresponding room-temperature solution

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* *Non-S.I. unit employed:* $G = 10^{-4}$ T.

Table. Phosphorus-31 chemical shifts in the solid and solution states[a]

Compound	Solution (20 °C)	Solution (−90 °C)	Solid state (20 °C)
$[Au_6\{P(C_6H_4Me\text{-}o)Ph_2\}_6][NO_3]_2$	46.5	52.6 (s, 2 P) 42.6 (s, 4 P)	57.9 (2 P) 48.6 (4 P)
$[Au_8\{P(C_6H_4OMe\text{-}p)_3\}_8][NO_3]_2$	44.3	—	70.9 (1 P) 51.9 49.0 (7 P)
$[Au_9\{P(C_6H_4OMe\text{-}p)_3\}_8][NO_3]_3$			
Golden-brown isomer	47.2	47.2[b]	58.2 (2 P) 52.0 (6 P)
green isomer	47.2	47.2[b]	63.2 (4 P) 50.9 (4 P)
$[Au_9\{P(C_6H_4OMe\text{-}p)_3\}_8][BF_4]_3$	50.7	50.7[b]	57.8 (2 P) 52.4 (6 P)
$[Au_{13}Br_4(PMePh_2)_8]Br$	44.0 (s, 4 P) 34.5 (t, 2 P) 32.0 (t, 2 P)	—	45.4[c] 41.2 37.1
$[Au_{13}(PMe_2Ph)_{10}Cl_2][PF_6]_3$	40.3	40.3	38.2

[a] All chemical shifts referenced to 85% H_3PO_4, with the convention that downfield shifts are positive. [b] Slight line broadening. [c] The relative intensities of the different peaks are not given because of overlap in spectra.

spectra. In order to understand the solid-state spectra, use was made of both the solution ^{31}P n.m.r. spectra and the molecular structures determined by *X*-ray diffraction studies. The Table summarises the relevant data.

The room-temperature solid-state spectrum of $[Au_6\{P(C_6H_4Me\text{-}o)Ph_2\}_6][NO_3]_2$ has two well-resolved peaks [Figure 1(*a*)]. The chemical shifts and relative intensities (1:2) of these resonances are closely similar to those observed in solution at low temperature (−90 °C).[8] The spectrum can readily be interepreted in terms of the structure of the cluster determined by *X*-ray diffraction, which can be described in terms of two edge-sharing tetrahedra of gold atoms. There are two different phosphorus environments, with two edge-sharing $Au{-}PR_3$ and four external $Au{-}PR_3$ fragments. As the temperature is increased above −90 °C the solution spectrum changes as the two resonances broaden and collapse into a single average resonance. There is therefore a marked difference in the solution and solid-state spectra at room temperature and this can be attributed simply to much faster intramolecular rearrangement processes in solution compared with those in crystals.

A similar conclusion is reached by a study of the n.m.r. spectra of the cluster $[Au_8\{P(C_6H_4OMe\text{-}p)_3\}_8][NO_3]_2$. The solid-state spectrum consists of one completely resolved peak at low field and a number, at least two, overlapping peaks at higher field [Figure 1(*b*)]. The solution spectrum at room temperature shows only one resonance.[8] Low-temperature solution spectra have not been run for this cluster, but they have been reported for the related cluster $[Au_8(PPh_3)_8]^{2+}$, which is isomorphous.[5] At low temperature, one resonance is found at low field at a chemical shift closely similar to that of the resolved resonance in the solid-state spectrum, and three other overlapping resonances were identified in the higher-field peak. The crystallographically imposed symmetry is C_{3v}, and therefore four different phosphine sites exist. One of these, the unique phosphine at the centre of the cluster, is markedly different from the remainder, having a longer Au–P distance (2.42 Å) than that of the others (2.29—2.33 Å), and the low-field resonance is assigned to this. Again, the difference between the solid-state and solution n.m.r. spectra at room temperature can be attributed primarily to the difference in rates of intramolecular rearrangement. In solution two distinct processes, involving the equilibration of all the phosphorus atoms and the movement of Au–P units around the central Au atom, have been identified; both of these are frozen out in the solid state.

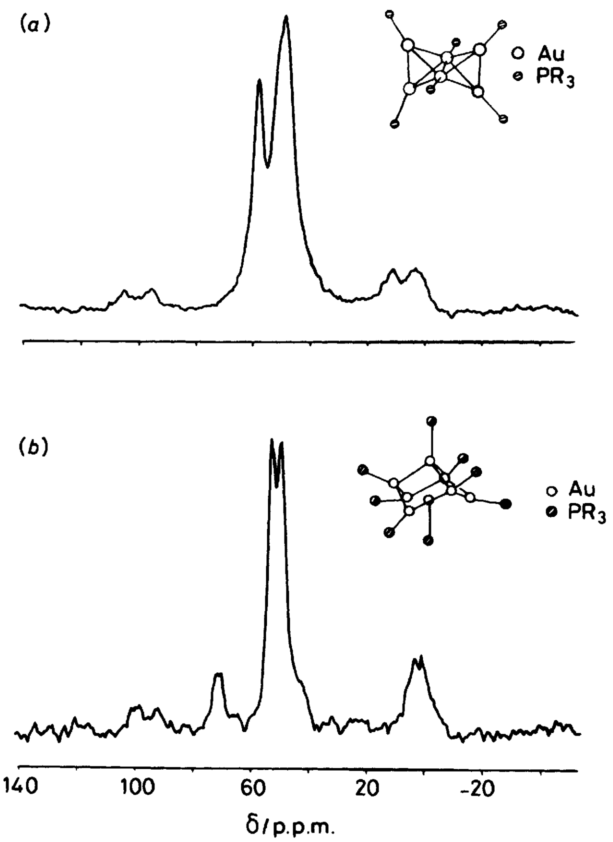

Figure 1. Solid-state ^{31}P n.m.r. spectra of (*a*) $[Au_6\{P(C_6H_4Me\text{-}o)Ph_2\}_6][NO_3]_2$ and (*b*) $[Au_8\{P(C_6H_4OMe\text{-}p)_3\}_8][NO_3]_2$

The cluster $[Au_9\{P(C_6H_4OMe\text{-}p)_3\}_8][NO_3]_3$ again gives rise to a single resonance in solution at room temperature, and although slight line broadening takes place no further splitting is observed even at low temperature.[9] Two crystal forms of the compound have been identified and characterised by single-crystal *X*-ray diffraction studies. The solid-state spectrum of one of these, the green isomer, shows two well resolved peaks of approximately equal intensity [Figure 2(*a*)]. The structure of

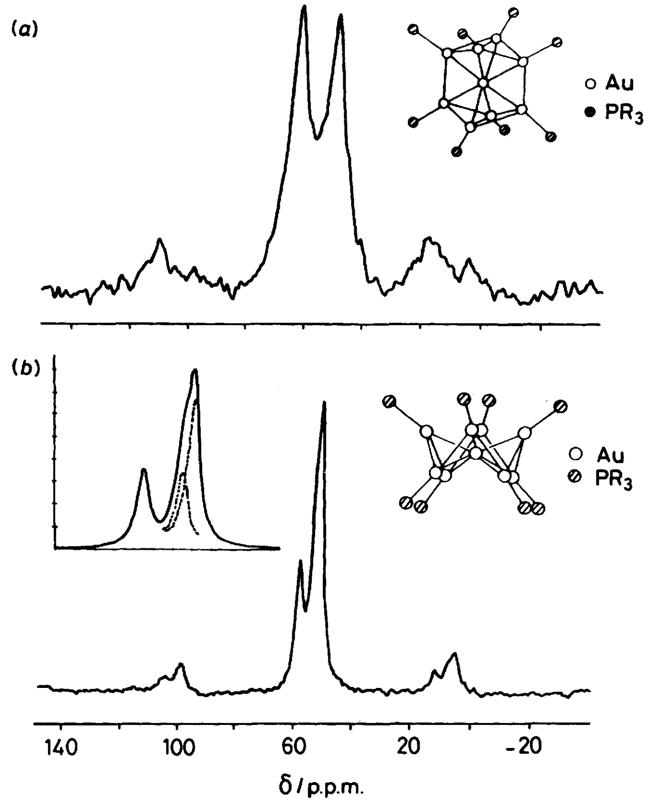

Figure 2. Solid-state ^{31}P n.m.r. spectra of $[Au_9\{P(C_6H_4OMe\text{-}p)_3\}_8][NO_3]_3$: (*a*) green isomer; (*b*) golden-brown isomer. Inset: simulation of spectrum with upfield peak taken to consist of two overlapping resonances with intensities in the ratio 1:2

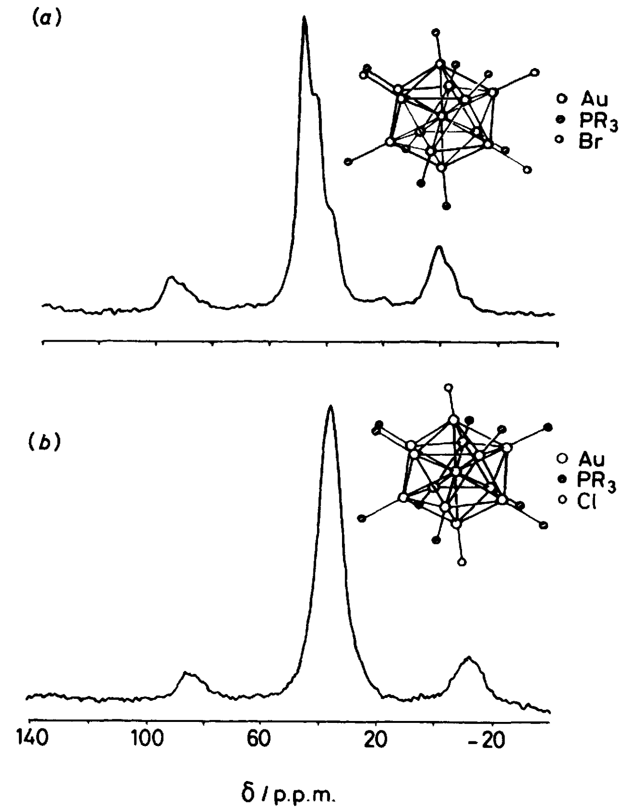

Figure 3. Solid-state ^{31}P n.m.r. spectra of (*a*) $[Au_{13}Br_4(PMePh_2)_8]Br$ and (*b*) $[Au_{13}(PMe_2Ph)_{10}Cl_2][PF_6]_3$

this isomer is based on a centred icosahedron from which a rectangle of gold atoms has been removed, thus giving two types of phosphorus site, each containing four ligands. This structure is completely consistent with the solid-state spectrum. The golden-brown isomer gives rise to two peaks with an intensity ratio of 1:3 [Figure 2(*b*)]. An identical spectrum is obtained for the BF_4^- salt, which has the same crystal structure as the brown isomer of the NO_3^- salt. The idealised skeletal symmetry of the cluster is a centred crown of gold atoms possessing D_{4d} symmetry, in which all of the phosphorus atoms are equivalent. The crystallographically imposed symmetry is only C_2, permitting four distinct phosphorus environments. The solid-state spectrum can therefore be explained by the overlap of the resonances of three nearly equivalent sites in the upfield resonance. The greater linewidth and asymmetry of this peak is consistent with this interpretation [see Figure 2(*b*)]. In solution, not only are the molecules undergoing fluxional processes, but rapid interconversion of isomers on the n.m.r. time-scale is also taking place.

The compound $[Au_{13}Br_4(PMePh_2)_8]Br$ is an example of a cluster which is stereochemically rigid in solution at room temperature. The solution spectrum consists of three resonances, in accord with the centred icosahedral structure shown in Figure 3(*a*).[8] The four bromine atoms produce three different phosphorus environments with four, two, and two ligands in each. Despite the overlap of resonances in the solid-state spectrum, three resonances at similar chemical shift values to those observed in the solution spectrum can be detected. Resolution enhancement by Gaussian multiplication leads to a clear resolution of the peaks.

The solid-state spectrum of $[Au_{13}(PMe_2Ph)_{10}Cl_2][PF_6]_3$ consists of a single phosphine resonance [Figure 3(*b*)]. The solution spectrum also shows only one line, but in this case it is not necessary to invoke stereochemical non-rigidity. The crystal structure is a centred icosahedron with chlorine atoms in the *para* positions.[11] All of the phosphorus atoms are equivalent in this idealised structure. There are, however, significant distortions to the icosahedron in the crystal, thus offering an explanation for the broad line (*ca.* 800 Hz) in the solid-state spectrum.

Discussion

In all of the clusters described above the structures in the solid state, at least of the cluster atoms, appear to be stereochemically rigid at room temperature. In solution all but one are non-rigid, and several are not frozen out at temperatures of −90 °C and below. This indicates the effect of intermolecular interactions in the crystal on intramolecular processes, and is in accord with previous observations on metal carbonyl clusters.[6,7] That this might not always be the case, however, is indicated by studies of $[Au_{11}(PMe_2Ph)_{10}][BPh_4]_3$. The solid-state n.m.r. spectrum consists of a single resonance. The crystal structure has not been determined because of crystallographic disorder, but the related $[Au_{11}I_3\{P(C_6H_4F\text{-}p)_3\}_7]$ has been structurally characterised and shown to have four chemically distinct phosphine environments.[15]

An important question for structure determination is whether intermolecular interactions affect the chemical shifts of the phosphines as well as their dynamic properties. The shifts would be affected by through-space interactions, for example ring-current shifts or electrostatic perturbations or by distortion of the geometry either of the cluster or of the phosphine substituents. The evidence from this work is that such effects are

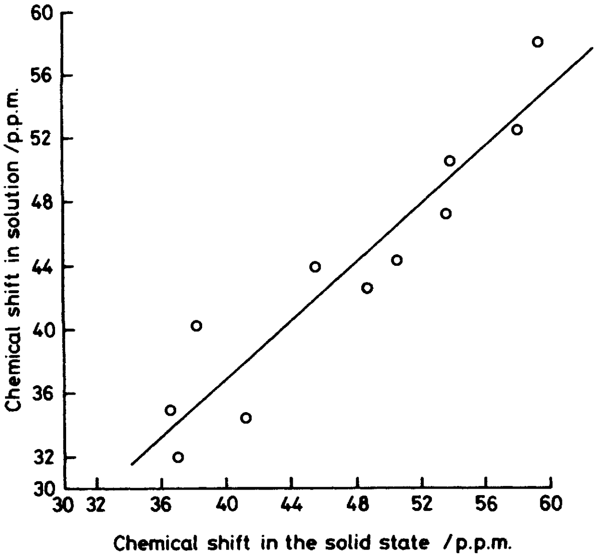

Figure 4. Plot of ^{31}P chemical shifts in the solid state against chemical shifts in solution. Low-temperature solution data were used where available. In cases where more resonances were observed in the solid state than in solution, an average value of the solid-state shifts weighted for the number of phosphines in each environment was plotted against the solution chemical shift. The solid line shows a least-squares fit to the data

observed, and that their existence cannot be ignored in structure determination. These results are in accord with those reported for various organic compounds based on n.m.r. studies using ^{13}C and other nuclei.[16] On average, the measured ^{31}P chemical shifts in the gold clusters are some 4.2 p.p.m. to higher field in the solid state compared with those in solution (see Table). A plot of the chemical shifts in solution against those in the solid state (Figure 4) demonstrates this, but shows that the correlation between the two sets of shifts is otherwise good.

Solid-state n.m.r. spectroscopy should therefore in general provide information for structural studies of molecules such as those examined here without the complication of the averaging of resonances through fluxional processes. That stereochemical rigidity is valuable for structural studies in the solid state is shown for example in the study of the isomers of $[Au_9\{P(C_6H_4OMe\text{-}p)_3\}_8][NO_3]_3$. Comparison of the spectra of the BF_4^- salt with those of the two isomers of the NO_3^- salt enables the molecular structure to be assigned without the need for diffraction studies. Other related clusters could be similarly examined in the solid state. Whether or not separate resonances are observed for each distinct phosphorus environment in the molecule depends on the resolution of the spectrum. In this work, the number of peaks represents a minimum value for the number of crystallographically distinct sites. The greater the difference in the environments, such as for example the Au–P bond lengths in $[Au_8\{P(C_6H_4OMe\text{-}p)_3\}_8][NO_3]_2$, the more likely is the resolution of the resonances. The results described here suggest that in many cases all of the distinct sites of the cluster framework will be resolved, but that the differences in, for example, phosphine rotameric sites will not be.

A combination of solid-state and solution n.m.r. spectroscopy appears particularly valuable in the study of phosphine-containing cluster compounds. One can make use of the combination of structural rigidity in the former and the high resolution of the latter for investigating both the structure and the dynamics of such clusters. The utility of the solid-state technique is likely to be of unique importance in cases where crystal structures cannot be determined. This may occur when suitable crystals cannot be obtained, or when the molecule of interest is contained in a non-crystalline environment, such as attached to a surface.

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