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AN EXAFS STUDY OF THE CLUSTER MOLECULE $Au_{55}(PPh_3)_{12}Cl_6$.

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Gold L_3 edge EXAFS has been used to study the coordination environment of gold atoms in the cluster molecule $Au_{55}(PPh_3)_{12}Cl_6$. The mean coordination of 7 by other gold atoms is consistent with a 3-shell cuboctahedral structure for the Au_{55} cluster. The first direct measurement of the Au-Au distance in this cluster shows that the spacing is significantly shorter than that in bulk metallic gold and is consistent with calorimetric work which has shown the Au-Au interactions are stronger in the cluster than in bulk gold. There is no evidence to suggest a significant spread of Au-Au distances in $Au_{55}(PPh_3)_{12}Cl_6$, in contrast to lower-nuclearity gold cluster molecules which have peripheral Au-Au distances typically 0.2Å longer than those to interstitial gold atoms.

1 Introduction.

The molecular compound $Au_{55}(PPh_3)_{12}Cl_6$ is prepared by reduction of $(PPh_3)AuCl$ with B_2H_6 in benzene. It has been characterised by methods including microanalysis and molecular weight determination using sedimentation measurements. ^{197}Au Mössbauer spectroscopy has shown the presence of different Au sites consistent with the proposed structure of a cuboctahedron with three concentric shells of metal atoms[1,2]. Images corresponding to 55-atom Au particles viewed along $< 110 >$ directions have been observed by high resolution electron microscopy[3]. This compound therefore represents an important molecular model for a small particle of Au[4].

There is increasing interest in the electronic structure of molecular metal clusters of this type[5]. Some of the spectroscopic[6,7] and electrical[8] properties of $Au_{55}(PPh_3)_{12}Cl_6$ have been found to be intermediate between those of lower-nuclearity gold clusters and colloidal gold.

However, $Au_{55}(PPh_3)_{12}Cl_6$ can be obtained in the solid state only as an amorphous powder unsuitable for X-ray crystallographic study. Consequently its molecular structure has not been directly determined and, in particular, no interatomic distances for the cluster have been available.

We have therefore used EXAFS to determine directly the coordination environment of the gold atoms in this molecule.

2 Experimental.

Two samples of $Au_{55}(PPh_3)_{12}Cl_6$ prepared at different times were ground to a fine powder and diluted with boron nitride powder so that any inhomegeneities in absorption across the area of the incident X-ray beam were minimised. The resulting mixtures were held in sample mounts consisting of 1mm thick aluminium plates into which a 5mm square aperture was cut. The optical path length of the X-rays transmitted through the sample was adjusted by stacking the sample containers to give a step of approximately unity in μt at the absorption edge.

The EXAFS measurements, at the Au L_3 edge were performed, at room temperature in air, on beamline 7.1 at the SRS, Daresbury Laboratory (DL). Monochromation of the incident X-ray beam was achieved using a double crystal Si(111) monochromator allowing rejection of higher order harmonics. Full beamline specifications are given elsewhere[9].

In addition to the measurements made on $Au_{55}(PPh_3)_{12}Cl_6$ an experiment was performed on a 10μm thick gold foil. The measurements made on this standard sample served three purposes, firstly the spectrum of the foil was used for monochromator calibration. Secondly the spectrum of the reference material was used for validation and empirical modification of the theoretically calculated electron phaseshifts used in the data analysis and finally the structural parameters obtained from bulk gold are useful for comparison with those measured for $Au_{55}(PPh_3)_{12}Cl_6$.

3 Data Analysis.

(i) Background subtraction.

The oscillatory part of the X-ray absorption coefficient is defined as

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\mu(E)} \qquad (1)$$

where $\mu_0(E)$ and μ(E) are the atomic absorption coefficients associated with the ejection of a core electron in an isolated atom and in an atom in the material of interest respectively. E is the energy of the photoelectron. The background subtraction and normalisation required to reduce the experimentally measured spectrum to χ(E) was achieved using the software package EXBACK[10] available at DL. Firstly the edge position is established from the position of the primary maximum in the first derivative of the absorption spectrum. Next the pre-edge background is fitted to a first order polynomial over a selected energy range, the function obtained is then extrapolated over the whole experimental energy range, this background can then be removed. A smooth function for μ_0(E) is obtained using a spline procedure in which three coupled, cubic polynomials are fitted to the post-edge spectrum. The knot positions are varied interactively until an acceptable function for μ_0(E) is obtained, special care being taken to ensure that the smooth background does not echo any of the frequency components of the EXAFS.

(ii) Data Fitting.

After background subtraction and normalisation the theoretical EXAFS function, $\chi(k)$, a simplified version of which is given in equation 2,

$$\chi(k) = \sum_{i=1}^{n} \frac{N_i}{kR_i^2} sin(2kR_i + 2\delta + \psi_i)|f(\pi,k)| exp-(A_i k^2) exp-\frac{2(VPI)R_i}{k} \qquad (2)$$

was fitted to the experimental spectrum using the rapid curved wave theory[11] implemented in the computer program EXCURV88[12]. Here $k = \frac{\sqrt{2mE}}{\hbar}$ is the magnitude of the photoelectron wave-vector. The summation in equation 2 refers to the number of atomic coordination shells contributing to the EXAFS, N_i is the number of atoms of type i occupying a shell of radius R_i. A_i is an effective Debye-Waller factor giving a representation of the static and thermal disorder of the system via a Gaussian distribution in interatomic spacings. The Debye-Waller factor is related to the mean square deviation in bond length σ (and hence the width of the Gaussian distribution) by

$$A = 2\sigma^2 \qquad (3)$$

δ and ψ are photo-electron phase-shifts, f(π,k) is the amplitude of the photo-electron backscattering factor and the parameter VPI is the imaginary part of the photoelectron self energy representing the effective mean free path of the photoelectron. An additional parameter included in the fitting procedure is an energy zero term, E_0, which accounts for any offset in the zero of the kinetic energy of the photoelectron from the position of the absorption edge.

Phase-shifts for both absorbing and scattering atoms were calculated using EXCURV88 and were then modified empirically using the spectrum of the Au foil to give good agreement with the known structure of bulk Au. Transferability of the phase-shifts between the Au and the Au_{55} samples was assumed.

Experimental spectra weighted by k^3 and best fits for bulk Au and both the Au_{55} samples are shown in figure 1. Also shown in this figure are the radial distribution functions (RDFs) obtained by Fourier transformation of the EXAFS functions. To minimise truncation effects caused by transforming over a finite data range a Gaussian window was using in the Fourier process. Changing the range over which transformation is performed is useful in distinguishing between real and spurious peaks in the RDF.

(iii) Error Analysis.

As some of the parameters evaluated in the fitting procedure are strongly correlated, care must be taken when estimating experimental errors. In figure 2 we show the relation between the fit index, FI, defined as

$$FI = \frac{1}{NPTS} \sum_{i=1}^{NPTS} (\chi(k)_{exp} - \chi(k)_{theory})^2 \qquad (4)$$

and some correlated structural parameters. As an estimate of the errors inherent in the experiment we have used the criterion

$$\frac{FI_{min}}{FI} = 0.96 \qquad (5)$$

shown as the bold contour in figure 2. This has been derived from statistical considerations[13] and gives a 95% probability that the correlated parameters lie within the region illustrated.

4 Discussion.

(i) Coordination number of the Au atoms.

The measured mean coordination numbers for the Au atoms in the $Au_{55}(PPh_3)_{12}Cl_6$ clusters are 7.0,7.3±2.5. This coordination number is an average taken over all of the Au sites in the cluster. The individual atoms in the cluster exhibit a variety of first neighbour coordination numbers depending on their positions. Assuming the cuboctahedral structure proposed for the core[1] and supported by Mössbauer spectroscopy[6,13] there are 5 distinct Au sites. Details of these sites and the coordination of the respective Au atoms are given in table 2.

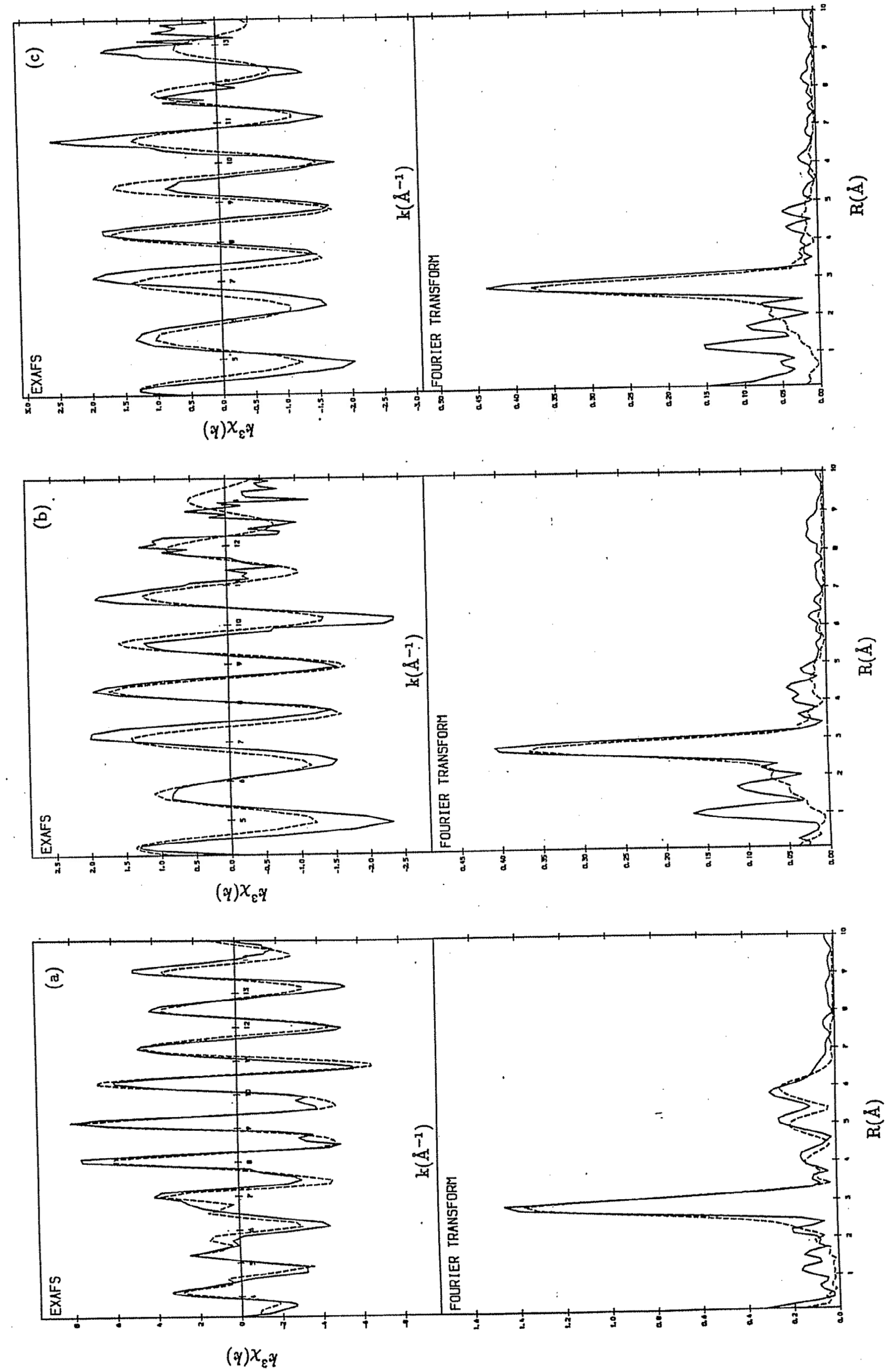

Figure 1. k^3 weighted EXAFS functions and radial distribution functions for bulk gold (a), sample 1 (b) and sample 2 (c). The solid curves are the experimental results and the broken curves represent the best fits to the data.

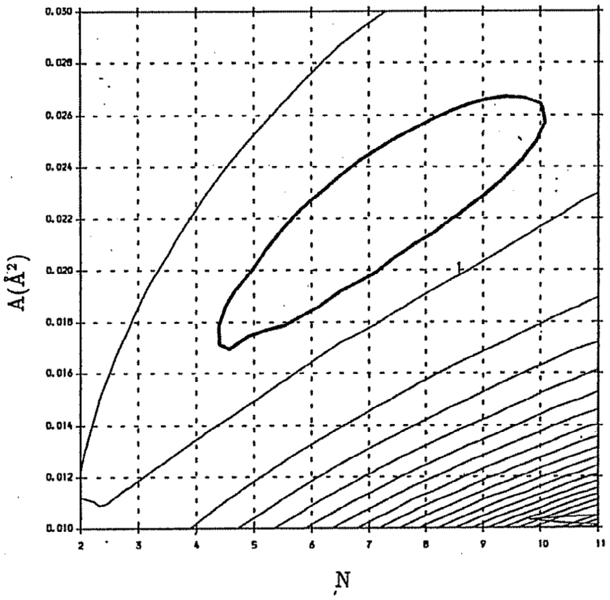

Figure 2. Contour map showing the relation between FI, N and A for sample 2. The 95% significance contour defined by equation 5 is emboldened.

Although the errors in coordination numbers obtained from this EXAFS experiment are large, the agreement of the measured value of the first neighbour coordination number and the value of 7.85 calculated from table 2 for the cubooctahedral model is encouraging. The presence of larger Au clusters would give a higher coordination number; even a four shell cuboctahedron has a first neighbour coordination number of 8.78 (table 3) while in colloidal Au particles the mean first neighbour coordination tends to that of the bulk (12). We also note that, whereas many lower-nuclearity Au cluster molecules have structures based on icosahedra[15], a 3-shell, 55 atom icosahedron would have a mean first neighbour coordination of 8.51. Our result may, therefore, be tentatively used to give further evidence for the cuboctahedral structure of $Au_{55}(PPh_3)_{12}Cl_6$.

(ii) Interatomic distances to Au atoms.

The measured nearest-neighbour Au-Au distances in the $Au_{55}(PPh_3)_{12}Cl_6$ samples are 2.76 and 2.78 ±0.02Å. This is the first direct measurement of an interatomic distance in this molecule. A much shorter Au-Au distance of 2.50Å which was derived from high-resolution electron microscopy[3] refers to the deliganded cluster

Table 1. Summary of structural parameters obtained from analysis of EXAFS data for bulk Au and the two Au_{55} cluster samples. The notation is that used in equation 2.

Parameter	Bulk Au	Au_{55} sample 1	Au_{55} sample 2
R(Å)	2.88±0.02	2.76±0.02	2.78±0.02
N	12.3±1	7.3±2.5	7.0±2.5
A	0.014±0.003	0.023±0.004	0.022±0.004

Table 2. Gold sites in the core of $Au_{55}(PPh_3)_{12}Cl_6$.

Gold site	Occupancy of site	Near neighbour coordination
PPh_3	12	5
Unbonded surface	24	7
Cl	6	8
Central atom	1	12
2nd central shell	12	12

Table 3. Average first neighbour coordination numbers for some cuboctahedral and icosahedral structures.

No. of shells	No. of atoms	Cuboctahedral	Icosahedral
2	13	5.54	6.46
3	55	7.85	8.51
4	147	8.98	9.47

which is present in vacuo in the electron beam and cannot be directly compared to our EXAFS measurement on $Au_{55}(PPh_3)_{12}Cl_6$ itself. Examination of the Debye-Waller factors obtained from the data fitting indicates that there is no significant increase in the width of the distribution of the Au-Au first neighbour distances in the cluster above that observed in bulk Au. The fitting parameter A is related to the mean square deviation in bond lengths, σ, by equation 3. This suggests a value of σ of 0.08Å for bulk Au and a σ of 0.11Å for the Au cluster.

No second or third neighbour Au-Au distances could reliably be refined from the EXAFS data for the Au_{55}. However, this result is not suprising for a number of reasons. In the Au_{55} cluster the mean outer shell coordination numbers are much lower than in bulk Au because of the small size of the cluster unit, moreover EXAFS measurements are biased towards the study of near-neighbour interactions primarily because of limitations on the electron mean free path.

No metal-ligand (Au-P or Au-Cl) correlations were measured in this experiment because of the extremely small average coordination of Au by the ligand atoms (P 0.22; Cl 0.11). Also, the ligand atoms only scatter the photoelectrons weakly because of their low atomic number. The peaks in the RDFs at distances below 2Å, where we may expect to observe Au-P and Au-Cl interactions, are caused by noise in the experimental spectra and by truncation effects in the Fourier transform. Direct measurement of the P and Cl environments, using SOXAFS, is not possible because the ligands are known to desorb in the high vacuum required for such an experiment[3].

The Au-Au distances measured for the cluster (2.76, 2.78 ±0.02Å) are considerably shorter than that in bulk Au (2.88Å)[16]. ^{197}Au Mössbauer isomer shifts had previously given tentative evidence that the Au-Au distances in the cluster core may be slightly longer than those in bulk Au[6,14]. Electron diffraction and Mössbauer measurements have shown that microcrystals of Au smaller than 3000Å in diameter have lattice spacings contracted from the bulk value[17]. The degree of Au-Au contraction we have measured in $Au_{55}(PPh_3)_{12}Cl_6$ is about that expected by extrapolation for a Au particle of this size. Our EXAFS result is also consistent with the conclusion of a calorimetric study of the decomposition of solid $Au_{55}(PPh_3)_{12}Cl_6$ into $(PPh_3)_2AuCl$ and metallic Au, which has shown that the individual Au-Au interactions in the cluster are substantially stronger (by about 25%) than in the bulk[7]. These results approximately fit the simple power law proposed for the dependence of the strength of the metal-metal bonds in clusters on their length[18]. The structures of many lower-nuclearity gold phosphine halide clusters containing up to 13 metal atoms have been determined by X-ray crystallographic methods[15]. Most of the clusters are based on 2-shell icosahedral structures. Their Au-Au bond lengths span a wide range from 2.6 to 3.2Å, but in many cases the mean Au-Au distance is close to 2.88Å. It is notable that bond lengths to interstitial gold atoms in these 2-shell clusters are closely similar to the values we have measured in $Au_{55}(PPh_3)_{12}Cl_6$. For example, in the highly symmetric icosahedral $[Au_{13}(PMe_2Ph)_{10}Cl_2]^{3+}$, the mean distance between peripheral and interstitial gold atoms is 2.77Å[19]. In the larger mixed metal cluster $[Ag_{12}Au_{13}(PPh_3)_{12}Cl_6]^{m+}$, which has a structure of three interpenetrating icosahedra, the mean $Au_{interstitial}$-$Au_{surface}$ distance is 2.72Å. There are two independent neighbouring interstitial gold atoms; the distance between them is 2.79Å[20].

In the 2 shell clusters, Au-Au distances on the cluster surface are generally longer, by typically 0.2Å, than those to the interstitial Au atom. In $[Au_{13}(PMe_2Ph)_{10}Cl_2]^{3+}$ the mean surface Au-Au distance is 2.91Å. There is no evidence from the EXAFS data for any such effect in the 3-shell $Au_{55}(PPh_3)_{12}Cl_6$. As 96 of the 216 nearest-neighbour distances in a 55-atom cuboctahedron are on the surface, any surface elongation would be certain at least to affect the value of σ for the Au-Au distance. The measured value of σ for the Au_{55} cluster (0.11Å) is not appreciably larger than that for bulk Au (0.08Å) suggesting only a small spread in interatomic distance, as opposed to the larger width for the distribution of bond lengths that would be present if interstitial and surface bond lengths were significantly different. In support of this EXAFS result, analysis of the thermal motion of the gold atoms in the cluster gave an excellent fit to specific heat and Mössbauer f-factor measurements using only a single parameter for the strength of the Au-Au interactions[14,21].

Two explanations may be proposed for the lack of surface elongation in $Au_{55}(PPh_3)_{12}Cl_6$. Firstly, in the 2-shell clusters every peripheral gold atom bears a ligand and there is severe steric repulsion between bulky phosphines on adjacent gold atoms. Steric effects are less important in $Au_{55}(PPh_3)_{12}Cl_6$ as there are only 18 ligands on 42 surface atoms; each Au atom bearing a ligand has for its nearest neighbour in the surface layer four Au atoms which are uncoordinated by ligands. Secondly, there are major electronic differences between the 3-shell cuboctahedral Au_{55} cluster and the 2-shell icosahedral clusters. Whereas bonding in the 2-shell clusters is dominated by radial interactions with the central gold atom, weaker tangential interactions occuring on the cluster surface[15], the bonding in $Au_{55}(PPh_3)_{12}Cl_6$ is much more delocalised and non-directional. There is good evidence for this from spectroscopic studies of gold cluster compounds. In $Au_{11}(PPh_3)_7Cl_3$, Mössbauer[14] and photoelectron spectroscopy[22] experiments have shown that the electronic environment of the central gold atom is quite different from that of an atom of bulk gold; the UV-visible spectra of 2-shell gold clusters show discrete one-electron transitions[15]. In contrast, the inner core Au atoms of $Au_{55}(PPh_3)_{12}Cl_6$ have Mössbauer parameters close to those of metallic gold[6,14] and UV-visible spectroscopy of this compound shows a broad absorption between 4.5 and 1.5eV which corresponds to the 5d→6s,6p interband transitions of colloidal gold[7]. The 520nm plasma resonance of delocalised conduction electrons, which is characteristic of colloidal gold with particle diameters down to 10Å[23] is also incipient in the absorption spectrum of $Au_{55}(PPh_3)_{12}Cl_6$. Recently, very high molecular weight palladium clusters have been synthesised which are believed to contain 6 concentric shells of metal atoms with an idealised nuclearity of 561[24,25]. An EXAFS study of one of these clusters[24] has given a uniform Pd-Pd distance of 2.60Å — shorter than the 2.75Å atomic spacing in bulk palladium[16] and also shorter than the mean Pd-Pd distances found by X-ray diffraction in lower-nuclearity palladium clusters. Thus a general feature of large metal cluster molecules may be emerging: that in clusters of sufficiently large size the delocalisation of bonding electrons leads to strong bonding with interatomic distances shorter than in the corresponding bulk metal.

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