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## Mössbauer Investigation and Novel Synthesis of Gold Cluster Compounds

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Mössbauer spectra of  $Au_{11}(PAR_3)_7X_3$  (Ar =  $C_6H_5$ ,  $p\text{-ClC}_6H_4$ ; X = SCN, I, CN) show different gold sites while an interpretation with five different gold sites (according to crystal structure) is possible. The peripheral gold atoms in the cluster are best described as linearly coordinated. A new way for the synthesis of these clusters was found; the evaporation of metallic gold into a solution of  $Au(PAR_3)X$  and  $PAR_3$  in ethanol resulted in a yield of 70% of the desired clusters.

### Introduction

Reactions of  $Au(PAR_3)X$  compounds with  $NaBH_4$  produce  $Au_{11}(PAR_3)_7X_3$  cluster compounds.<sup>1</sup> The yields of these reactions have not been reported but we found them to be low. A new technique described in this article for the preparation of these cluster compounds gives substantially higher yields.

Preliminary results of the crystal-structure determinations of  $Au_{11}[P(C_6H_5)_3]_7(SCN)_3$  and  $Au_{11}[P(p\text{-ClC}_6H_4)_3]_7I_3$  and the complete crystal structure of  $Au_{11}[P(p\text{-FC}_6H_4)_3]_7I_3$  have been reported.<sup>2-4</sup> In the latter compound (see Figure 1) a central gold atom is surrounded by ten peripheral gold atoms at distances varying from 2.60 to 2.71 Å. The distances between the peripheral gold atoms are in the range of 2.84–3.19 Å (mean 2.98 Å) and their interactions are therefore considered to have bonding character.<sup>1,4</sup>

X-ray photon electron spectra (XPS) reported by Battistoni et al.<sup>5</sup> seemed to implicate a large electron delocalization over the gold atoms, because only one absorption corresponding with the  $Au(4f)$  ionization energy was observed.

However, a molecular orbital calculation performed by Mingos<sup>6</sup> indicated large differences in the atomic charge of the various gold atoms within a  $Au_{11}^{3+}$  cluster. The same calculation also led to the conclusion that, apart from the radial interactions between the peripheral atoms and the atom at the center of the polyhedron, the somewhat weaker metal-metal bonds on the periphery of the polyhedron make an important contribution to the cluster stability. We have taken Mössbauer spectra of several  $Au_{11}$  cluster compounds to gain more insight in the bonding of the gold atoms.

### Experimental Section

The gold cluster compounds were prepared by the  $NaBH_4$  method described in the literature<sup>7</sup> and by means of a metal evaporation technique. For the evaporation experiments a rotary apparatus introduced by Timms<sup>8</sup> was used. Gold metal was evaporated from a resistively heated tungsten boat into an ethanol film of  $-100^\circ C$  containing  $Au(PAR_3)X$  and  $PAR_3$ . The ratio of the reactants was  $Au:Au(PAR_3)X:PAR_3 = 8:3:4$ . The pressure in the continuously pumped 1-L flask of the rotary apparatus could be kept at about  $10^{-2}$  Torr. After completion of the metal evaporation, the solvent was removed in vacuo. Subsequently, the residue was crystallized from methylene chloride-ethanol. Some of the products were identified through comparison of their cell dimensions with those reported in the literature but in most cases the infrared spectrum, elemental analysis, and the color of the product were used for identification.

The Mössbauer spectra were recorded at 4.2 K with an apparatus described earlier.<sup>9,10</sup> The integrating counting technique was used.<sup>11</sup> From each measurement two spectra, which were analyzed independently, were obtained due to the application of a triangular variation of the velocity. The spectrum of  $Au_{11}[P(C_6H_5)_3]_7(CN)_3$  was also measured at 25 K, but apart from a sharp decrease of intensity no

significant change in the spectrum was observed.

### Results

**Preparation of Gold Clusters.** The yields obtained with the metal evaporation technique were much higher than those obtained with the  $NaBH_4$  method (e.g., 60–70% vs. 10–20%, respectively, for  $Au_{11}(PPh_3)_7(SCN)_3$  (Ph =  $C_6H_5$ )).

Apart from the preparation route described above,  $Au_{11}(PPh_3)_7(SCN)_3$  could also be prepared through evaporation of gold into an ethanolic solution of KSCN and  $PPh_3$ . From the latter reaction  $Au(PPh_3)_2SCN$  could be isolated as a by-product, obviously as a result from the oxidation of Au in the solution of  $PPh_3$  and KSCN in ethanol.  $Au(O_2)$ , recently reported by McIntosh,<sup>12</sup> might be an intermediate in this oxidation reaction. Formation of this intermediate is possible because of the air flow through the system. Subsequent reaction of  $Au(PPh_3)_2SCN$  with Au leads to  $Au_{11}(PPh_3)_7(SCN)_3$ . The earlier described cluster compounds  $Au_9(PPh_3)_8(PF_6)_3$  and  $Au_9[P(p\text{-MeC}_6H_4)_3]_8(PF_6)_3$ <sup>13</sup> could also be prepared by the evaporation technique via the reaction of  $Au(PAR_3)_2NO_3$  and  $PAR_3$  with gold in ethanol ( $Au(PAR_3)_2NO_3:PAR_3:Au = 3:2:6$ ). Addition of  $NH_4PF_6$  results in the precipitation of the  $Au_9$ -cluster compounds with a 60% yield. Mössbauer spectra of these compounds will be reported later.

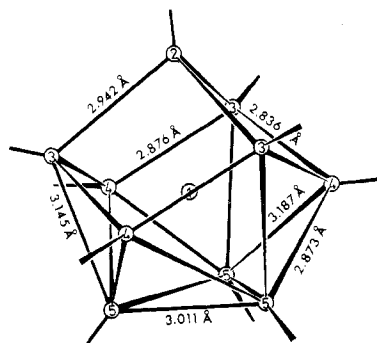
**Mössbauer Spectra.** The Mössbauer spectra of  $Au_{11}(PAR_3)_7X_3$  with Ar =  $p\text{-ClC}_6H_4$  and X = SCN, I, and CN are given in Figure 2. Practically the same spectra were obtained for the corresponding  $PPh_3$  compounds. In the crystal structures of the  $Au_{11}$  clusters five different gold sites can be distinguished<sup>2-4</sup> (see Figure 1). Each site can give rise to one quadrupole pair of Mössbauer absorption lines. To reduce the number of parameters we made the following assumptions:

(a) To account for saturation broadening the line width of all absorptions is taken as 2.00 mm/s which is slightly more than the natural line width (1.86 mm/s).

(b) For each of the peripheral gold atoms at sites 2, 3, 4, and 5 (see Figure 1), the intensities were assumed to be equal whereas the intensity for the central gold atom is allowed to be different. This is reasonable as the Mössbauer absorption intensity is proportional to  $\exp(-\langle x^2 \rangle_T)$ , where  $\langle x^2 \rangle_T$  is the mean-squared vibration amplitude at temperature  $T$ .

(c) Because of the almost spherical environment of the central gold atom we assume that the quadrupole splitting of this atom is zero.

The number of parameters is thus reduced to eleven: nine line-position parameters and two intensities. This number can be further reduced assuming that variation of X ligands at site 4 has a negligible influence upon the other gold sites. Thus,



**Figure 1.** Structure of gold cluster in  $\text{Au}_{11}[\text{P}(p\text{-FC}_6\text{H}_4)_3]_7\text{I}_3$ . Distances between central and peripheral gold atoms: Au(2), 2.600 Å; Au(3), 2.680 Å; Au(4), 2.718 Å; Au(5), 2.671 Å. Sites 2, 3, and 5 are coordinated to  $\text{PAR}_3$  and site 4 is coordinated to the X ligand, as discussed in the text.

**Table I.** Positions of Lines Corresponding with Au-X Sites As Derived from Difference Spectra<sup>a</sup>

Difference spectrum	Site	Position, mm/s
$\text{Au}_{11}[\text{P}(p\text{-ClC}_6\text{H}_4)_3]_7(\text{I} - \text{SCN})_3$	SCN	3.12
	I	1.95
$\text{Au}_{11}[\text{P}(p\text{-ClC}_6\text{H}_4)_3]_7(\text{CN} - \text{SCN})_3$	SCN	2.65
	CN	5.20
$\text{Au}_{11}[\text{P}(p\text{-ClC}_6\text{H}_4)_3]_7(\text{CN} - \text{I})_3$	I	2.06
	CN	5.16

<sup>a</sup> Position is given with respect to the  $^{197}\text{Pt}$  source.

the difference of two spectra of cluster compounds in which X (at site 4) is varied gives the positions of the absorptions corresponding with this site. After application of an appropriate scaling factor, the difference spectra were obtained numerically and fitted with two Lorentzians, one with positive and one with negative intensity. An example of such a difference spectrum is given in Figure 3. Results of these fits are given in Table I for  $\text{Au}_{11}[\text{P}(p\text{-ClC}_6\text{H}_4)_3]_7\text{X}_3$ . The line positions thus found were kept fixed in the further analysis of the spectra. The results of such least-squares fits using eight line-position parameters are given in Figure 2.

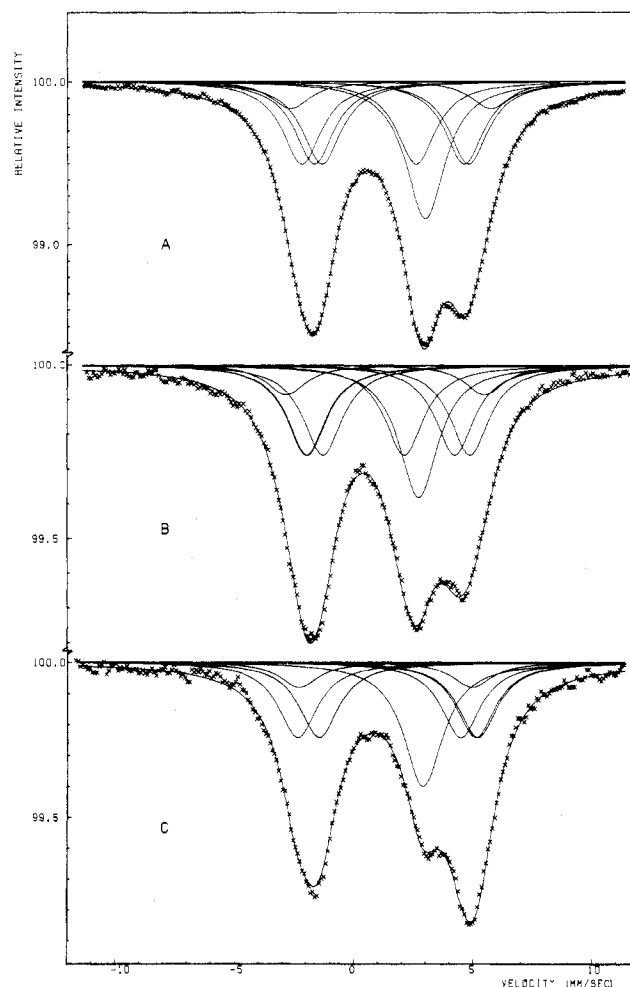
In Table II the quadrupole splittings (QS) and isomer shifts (IS) of the various pairs for all six compounds are given. The data are the average of the results of the two spectra obtained in one measurement.

A unique assignment of the lines at the left-hand side of the spectra to the sites 3, 4, and 5 is not possible. The actual choice was made such that QS and IS for  $\text{PAR}_3$ -coordinated gold were changing as little as possible for different X ligands. Because of the small intensity the line positions for site 2 are rather uncertain. The difference between compounds with the same X ligand but different Ar groups is small in most cases. In Table III we summarize the results by giving QS and IS for the various sites as a function of the coordinating ligand. The ratio of the intensity per gold atom for the central and peripheral gold atoms is fairly constant in all spectra and equal to  $2.3 \pm 0.2$ .

**Table II.** QS and IS of  $^{197}\text{Au}$  at Various Sites in  $\text{Au}_{11}(\text{PAR}_3)_7\text{X}_3$ <sup>a</sup>

	IS, mm/s				QS, mm/s			
	1	2	3 and 5	4	1	2	3 and 5	4
$\text{Au}_{11}(\text{PPh}_3)_7(\text{CN})_3$	2.94	0.14	1.46, 1.87	1.40	0	5.84	6.08, 6.56	7.55
$\text{Au}_{11}(\text{PPh}_3)_7(\text{SCN})_3$	2.68	0.54	1.09, 2.11	0.15	0	7.55	6.26, 6.39	4.70
$\text{Au}_{11}(\text{PPh}_3)_7\text{I}_3$	2.85	1.70	1.40, 1.74	0.00	0	9.13	6.04, 6.18	4.12
$\text{Au}_{11}[\text{P}(p\text{-ClC}_6\text{H}_4)_3]_7(\text{CN})_3$	2.90	0.70	1.54, 1.79	1.41	0	6.45	5.99, 6.51	7.55
$\text{Au}_{11}[\text{P}(p\text{-ClC}_6\text{H}_4)_3]_7(\text{SCN})_3$	2.95	1.18	1.51, 1.77	0.20	0	7.84	6.17, 6.42	4.80
$\text{Au}_{11}[\text{P}(p\text{-ClC}_6\text{H}_4)_3]_7\text{I}_3$	2.74	1.37	1.21, 1.75	0.00	0	8.42	6.12, 6.23	4.12

<sup>a</sup> Isomer shift is given with respect to the  $^{197}\text{Pt}$  source.

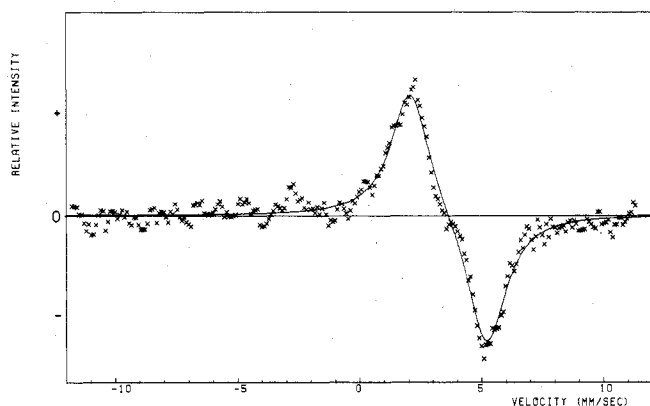


**Figure 2.** Mössbauer spectra of  $\text{Au}_{11}[\text{P}(p\text{-ClC}_6\text{H}_4)_3]_7\text{X}_3$ : (A) X = SCN, (B) X = I, (C) X = CN.

## Discussion

From the spectra it follows that the gold atoms in the  $\text{Au}_{11}$  clusters have very different electronic structures depending on the coordinating ligands.

Table IV gives the Mössbauer parameters of some monovalent gold compounds with the same ligands as in the  $\text{Au}_{11}$  clusters. These data were taken from a recent extensive Mössbauer study on gold complexes.<sup>10</sup> When these results are compared with those obtained for the clusters, it can be seen that there is a close correlation: (a) gold compounds in which I or SCN is coordinated have approximately the same IS and QS; (b) substitution of the halogen by  $\text{PPh}_3$  or CN results in an increased QS and IS (compare  $(\text{ClAuCl})^-$  with  $\text{Au}(\text{PPh}_3)\text{Cl}$  and  $\text{Au}(\text{PPh}_3)\text{SCN}$  with  $\text{Au}(\text{PPh}_3)\text{CN}$ ); (c) plots of QS vs. IS for monovalent linearly coordinated gold complexes give an almost linear correlation.<sup>10,14,15</sup> The values found for the peripheral atoms in the cluster compounds appear to follow the same IS/QS relation.



**Figure 3.** Difference spectrum obtained by subtracting the spectrum of  $\text{Au}_{11}[\text{P}(p\text{-ClC}_6\text{H}_4)_3]_7\text{I}_3$  (Figure 2B) from that of  $\text{Au}_{11}[\text{P}(p\text{-ClC}_6\text{H}_4)_3]_7(\text{CN})_3$  (Figure 2C). The line with negative intensity corresponds with a line in the spectrum of the CN compound, not present in the I compound, and vice versa. The drawn line is a fit with two Lorentzians of almost equal but opposite intensity at positions 2.06 mm/s (positive) and 5.16 mm/s (negative). The small structure around -3 mm/s was neglected.

**Table III.** QS and IS for Different Gold Sites in  $\text{Au}_{11}(\text{PAR}_3)_7\text{X}_3^a$

Site	QS, mm/s	IS, mm/s
Au(1)		$2.8 \pm 0.2$
Au(2)	$7.5 \pm 1.5$	$1.0 \pm 1.0$
Au(3), Au(5)	$6.1 \pm 0.2$ $6.4 \pm 0.2$	$1.4 \pm 0.2$ $1.8 \pm 0.2$
Au(4)-CN	$7.6 \pm 0.2$	$1.4 \pm 0.2$
Au(4)-SCN	$4.8 \pm 0.2$	$0.2 \pm 0.2$
Au(4)-I	$4.1 \pm 0.2$	$0.0 \pm 0.2$

<sup>a</sup> Uncertainties are estimated, based on results given in Table II. Isomer shift is with respect to  $^{197}\text{Pt}$  source.

**Table IV.** QS and IS for Some Gold Compounds<sup>a</sup>

Site	QS, mm/s	IS, mm/s
$\text{Ph}_3\text{P-Au-CN}$	10.11	3.82
$\text{Ph}_3\text{P-Au-SCN}$	7.65	2.85
$\text{Ph}_3\text{P-Au-I}$	7.35	2.77
$\text{Ph}_3\text{P-Au-Cl}$	7.49	2.93
$(\text{Cl-Au-Cl})^-$	6.43	0.74

<sup>a</sup> Isomer shift is with respect to  $^{197}\text{Pt}$  source.

For these reasons we believe that the peripheral gold atoms are best described as linearly coordinated gold atoms (Au-Au-X) which are strongly bound to the central gold atom but have only weak direct bonds (if any) between the peripheral gold atoms. Important direct (two center) interactions between the peripheral gold atoms would result in reduced quadrupole splitting and a distinct deviation from the IS/QS relation found for linearly coordinated Au(I).

The short peripheral gold-gold distances (mean 2.98 Å) do not necessarily imply an important interaction: the dimer bis(dipropyldithiocarbamatogold) contains two gold atoms at a distance of 2.75 Å.<sup>16</sup> However, Raman<sup>17</sup> and Mössbauer spectra<sup>10</sup> give no evidence of a strong gold-gold interaction. Bonding interactions between peripheral gold atoms via three-center two-electron bonds with the central atom, however, cannot be excluded.

### Conclusions

Metal evaporation proved to be a useful technique for the synthesis of gold cluster compounds. The reaction circumstances are much simpler than in cases where reductants such as  $\text{NaBH}_4$  have to be added. From the Mössbauer measurement it can be concluded that there are electronically different gold sites in the  $\text{Au}_{11}$  clusters: (1) the central gold atom, (2) peripheral gold atoms coordinated to X ligands, and (3) peripheral gold atoms coordinated to  $\text{PAR}_3$ . Further it can be concluded that the cluster compounds can be thought to consist of linearly coordinated Au units with the central gold atom as common ligand. Interactions between the peripheral gold atoms are small.

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**Registry No.**  $\text{Au}_{11}(\text{PPh}_3)_7(\text{CN})_3$ , 34247-61-5;  $\text{Au}_{11}(\text{PPh}_3)_7(\text{SCN})_3$ , 12583-03-8;  $\text{Au}_{11}(\text{PPh}_3)_7\text{I}_3$ , 34390-38-0;  $\text{Au}_{11}[\text{P}(p\text{-ClC}_6\text{H}_4)_3]_7(\text{CN})_3$ , 65982-54-9;  $\text{Au}_{11}[\text{P}(p\text{-ClC}_6\text{H}_4)_3]_7(\text{SCN})_3$ , 65982-55-0;  $\text{Au}_{11}[\text{P}(p\text{-ClC}_6\text{H}_4)_3]_7\text{I}_3$ , 12582-97-7.

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