Structural Characterisation of Two Crystalline Modifications of $[Au_9\{P(C_6H_4OMe\text{-}p)_3\}_8](NO_3)_3$: the First Example of Skeletal Isomerism in Metal Cluster Chemistry

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$[Au_9\{P(C_6H_4OMe\text{-}p)_3\}_8](NO_3)_3$ crystallises from CH_2Cl_2–toluene in two crystalline modifications one tetragonal and the other orthorhombic; single crystal *X*-ray crystallographic determinations on the two modifications have demonstrated that the tetragonal modification has a skeletal geometry derived from an icosahedron and the orthorhombic modification a centred crown skeletal geometry.

Since 1980 it has become apparent that some transition metal cluster compounds may have alternative skeletal geometries which differ by only small energy differences. In particular solution n.m.r. studies have suggested that the cluster compounds $[Rh_9P(CO)_{21}]^{2-}$,[1] $[Au_9(PPh_3)_8]^{3+}$, and $[Au_{11}Cl_3(PPh_3)_7]$[2,3] are stereochemically non-rigid and undergo facile skeletal rearrangements. In addition Lewis and Johnson[4] have noted that the skeletal geometries of metal carbonyl cluster anions can undergo dramatic rearrangements on protonation, *e.g.* $[Os_6(CO)_{18}]^{2-}$ is octahedral, but $[Os_6H_2(CO)_{18}]$ is capped square-pyramidal. However, prior to this work there have not been any well characterised examples of clusters exhibiting skeletal isomerism, *i.e.* compounds having the same stoicheiometries but different skeletal geometries in the solid state.[4]

Our recent observation that $[Au_9\{P(C_6H_4OMe\text{-}p)_3\}_8](BF_4)_3$ has centred crown geometry[5] in contrast to $[Au_9\{P(C_6H_4Me\text{-}p)_3\}_8](PF_6)_3$ which has a D_{2h} skeletal geometry derived from an icosahedron,[6] suggested that a change in the counter-anion could lead to the isolation of skeletal isomers.

When $[Au_9\{P(C_6H_4OMe\text{-}p)_3\}_8](NO_3)_3$, which was obtained in 90% yield from $Au(NO_3)P(C_6H_4OMe\text{-}p)_3$ and $NaBH_4$, was recrystallised from CH_2Cl_2–toluene it was noted that two modifications co-crystallised. The two types of crystals were easily separated on the basis of their colour. The green modification had a diffuse reflectance electronic spectrum very similar to that reported previously for $[Au_9\{P(C_6H_4Me\text{-}p)_3\}_8](PF_6)_3$ (D_{2h} skeletal geometry) and the golden brown modification had spectral characteristics similar to those reported for $[Au_9\{P(C_6H_4OMe\text{-}p)_3\}_8](BF_4)_3$

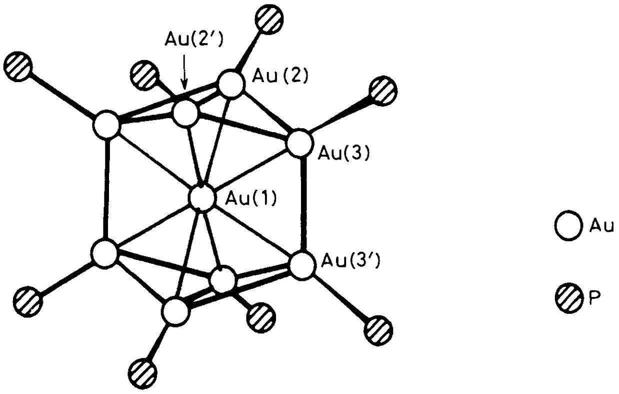

Figure 1. Skeletal geometry of the cluster cation in the green tetragonal modification of $[Au_9\{P(C_6H_4OMe\text{-}p)_3\}_8](NO_3)_3$. Important bond lengths are: Au(1)–Au(2) 2.689(2), Au(1)–Au(3) 2.735(2), Au(2)–Au(2′) 2.751(4), Au(3)–Au(3′) 2.783(4), Au(2)–Au(3) 2.866(4), and Au(2′)–Au(3) 2.899(4) Å. The cation lies on a special position with 222 symmetry.

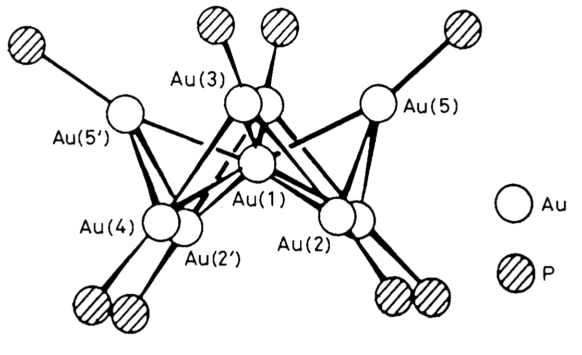

Figure 2. Skeletal geometry of the cluster cation in the golden brown orthorhombic modification of $[Au_9\{P(C_6H_4OMe\text{-}p)_3\}_8](NO_3)_3$. Important bond lengths are: Au(1)–Au(2) 2.677(2), Au(1)–Au(3) 2.676(2), Au(1)–Au(4) 2.659(2), Au(1)–Au(5) 2.659(2), Au(2)–Au(3) 2.843(3), Au(3)–Au(4) 2.810(3), Au(4)–Au(5') 2.825(3), and Au(5)–Au(2) 2.814(3) Å. The cation lies on a two fold axis of symmetry.

(crown skeletal geometry).[5] Confirmation that the green and golden brown modifications represent skeletal isomers has been obtained by single crystal *X*-ray crystallographic determinations.[†]

Although high quality crystals of the two modifications could not be obtained the task of establishing that they represent examples of skeletal isomerism was considerably simplified because they proved to be isomorphous with $[Au_9\{P(C_6H_4Me\text{-}p)_3\}_8](PF_6)_3$, which crystallises in the tetragonal space group $P\bar{4}n2$[6] and $Au_9\{P(C_6H_4OMe\text{-}p)_3\}_8](BF_4)_3$ which crystallises in the orthorhombic space group *Pbcn*.[5] The refined atomic positions for the two modifications of the NO_3^- salt proved to be very similar to those reported previously.[5,6]

The structures of the cluster cations are illustrated in Figures 1 and 2. The green (tetragonal) modification has a D_{2h} geometry derived from the icosahedron by the removal of a rectangle of metal atoms and the golden brown (orthorhombic) modification has a centred crown geometry. Therefore, the crystallographic analyses have confirmed that the two modifications represent the first examples of skeletal isomerism. The more open structure observed for the centred crown is reflected in the calculated volumes per cluster for the two structures, 4232 Å^3 for centred crown *vs.* 4098 Å^3 for the D_{2h} structure.

The bond lengths in the cluster cations are very similar to those reported previously for these skeletal geometries.[5,6] The radial Au–Au bond lengths in the tetragonal modification lie in the range 2.689(2)—2.735(2) Å with a mean of 2.712(23) Å. The comparable lengths in the orthorhombic modification lie in the range 2.659(2)—2.677(3) Å with a mean of 2.668(6) Å. The peripheral Au–Au distances in the former fall between 2.751(4) and 2.899(4) Å and show a greater variation from the mean [2.825(35) Å] than those for the orthorhombic modification 2.810(3)—2.843(3) Å [mean 2.823(7) Å]. This can be attributed to the greater steric strain imposed on the skeleton by the bulky ligands in the more compact tetragonal structure.

In solution both crystalline modifications give electronic spectra with identical characteristics and show an identical resonance in their $^{31}P\{^1H\}$ spectra at 50.7 p.p.m. (with respect to trimethylphosphate at 303 K). These observations suggest that the isomers share a common structure in solution. Little line broadening and no additional fine structure were observed in the $^{31}P\{^1H\}$ spectrum even at 200 K suggesting that in solution either the cluster adopts a structure which has all phosphine ligands equivalent, or a rapid rearrangement process is making them equivalent on the n.m.r. time scale.

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[†] *Crystal data*: green modification, $C_{168}H_{168}Au_9O_{24}P_8 \cdot 3(NO_3)$, M = 4777.8, tetragonal, $P\bar{4}n2$ (Space group No. 118), a = 19.566(7), c = 21.412(7) Å, U = 8 196 Å^3, Z = 2, D_c = 1.94 g cm^{-3}, $F(000)$ 4584 electrons, μ(Mo-$K_{\bar{\alpha}}$) 84.21 cm^{-1}, 3326 reflections were measured on an Enraf–Nonius CAD4F diffractometer in the range $3.0 \leqslant 2\theta \leqslant 30°$. The structure was solved by Patterson and Fourier methods and refined by block matrix least-squares [Au, P(1) anisotropic, P(2), C, N, O isotropic] to $R = 0.080$ for 1579 unique observed reflections [$I \geqslant 3\sigma(I)$]. The atomic co-ordinates of the atoms in the cluster cation are virtually identical with those reported previously for $Au_9\{P(C_6H_4Me\text{-}p)_3\}_8](PF_6)_3$.[6] One nitrate anion was located at special position *e* (site symmetry 2). Residual electron density (1—2.5 e Å^{-3}) suggested that the remaining nitrate anion was grossly disordered.

Golden brown modification, orthorhombic, space group *Pbcn*, a = 30.892(6), b = 17.522(7), c = 31.272(10) Å, U = 16 927 Å^3, Z = 4, D_c = 1.87 g cm^{-3}, $F(000)$ 9168 electrons, μ(Cu-$K_{\bar{\alpha}}$) 158.06 cm^{-1}, 3352 reflections were measured in the range $4.0 \leqslant 2\theta \leqslant 60°$, λ(Cu-K_α) radiation 1.5418 Å. The structure was solved by Patterson and Fourier methods and refined by block matrix least-squares (Au, P anisotropic, C,N,O isotropic) to R = 0.050 for 1793 unique reflections having $I \geqslant 3\sigma(I)$. The atomic co-ordiantes of the cluster are virtually identical to those reported previously for $[Au_9\{P(C_6H_4OMe\text{-}p)_3\}_8](BF_4)_3$.[5]

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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