

Synthesis and Microcrystal Structure Determination of $[\text{Au}_{10}(\text{PPh}_3)_7\{\text{S}_2\text{C}_2(\text{CN})_2\}_2]$ with Monochromatic Synchrotron Radiation

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The structure of this high nuclearity gold cluster has been determined from a single microcrystal of dimensions $10 \times 10 \times 30 \mu\text{m}$ (the X-ray diffraction data were recorded with synchrotron radiation using an Enraf-Nonius area detector diffractometer at Daresbury Laboratory); in the cluster three trigonal bipyramidal Au_5 groups share a common central gold atom and share edges; the group of ten gold atoms has symmetry near to D_{3h} , but when the seven triphenyl phosphine and two dithiolene ligands are taken into account the molecular symmetry is very approximately C_2 .

Synchrotron radiation with the FAST diffractometer has been shown to be useful for structure determination of small single crystals.¹⁻⁴ The characterization of high nuclearity cluster compounds still depends heavily on the determination of their structures by single crystal X-ray diffraction techniques, despite recent developments in FAB mass spectrometry, NMR and EXAFS.⁵ Conventional X-ray techniques normally require single crystals with dimensions of the order of $(0.1 \text{ mm})^3$ —300 times the volume of the largest crystals available in this case.

As part of a more general study of the reactivity of gold cluster compounds⁶ the reaction of $[\text{Au}_9(\text{PPh}_3)_8](\text{NO}_3)_3$ with an excess of $\text{Na}_2\text{S}_2\text{C}_2(\text{CN})_2$ in methanol was investigated, and yielded an initial brown precipitate, subsequently characterised as $[\text{Au}_8(\text{PPh}_3)_7][\text{S}_2\text{C}_2(\text{CN})_2]$. This brown precipitate, on recrystallisation from CH_2Cl_2 -MeCN, gave dark-brown crystals of $[\text{Au}_{10}(\text{PPh}_3)_7\{\text{S}_2\text{C}_2(\text{CN})_2\}_2]$, **1**, in 45% yield.[†] Repeated attempts to grow sufficiently large crystals for conventional X-ray structure determination failed; the spectroscopic and mass spectral data were not sufficiently unambi-

guous to define the stoichiometry and structure of the compound.

With a conventional sealed X-ray tube and CAD-4 diffractometer these crystals gave weak diffraction, totally inadequate for structure determination. At SERC Daresbury Laboratory, with the intense wiggler beam on workstation 9.6, it was possible to record a much more extensive diffraction pattern, and process it to give the unit cell and then 6470 unique reflection intensities.[‡] These reflection intensities were sufficient to give, by direct methods (SHELXS7), the positions of ten heavy atoms, assumed to be Au. Fourier and difference-Fourier syntheses revealed the complete structure. No evidence was found for any solvent of crystallisation or counter-ion molecules in the residual electron density.

The structure of **1** may be described as three trigonal bipyramidal Au_5 clusters sharing a common central gold atom and edge sharing. The gold atoms define a skeleton with idealised D_{3h} geometry, but the presence of the two bidentate dithiolene ligands reduces the symmetry of the cluster to C_2 . A similar skeletal geometry has been reported previously⁸ for $[\text{Au}_{10}\text{Cl}_3(\text{Pcy}_2\text{Ph})_6](\text{NO}_3)$ which formed in low yield from $[\text{Au}(\text{NO}_3)(\text{Pcy}_2\text{Ph})]$ and NaBH_4 (cy = cyclohexyl). Compound **1** is unusual because unlike other high nuclearity gold cluster compounds which have only one terminal ligand coordinated to each peripheral gold atom, it has bidentate dithiolene ligands. Therefore although $[\text{Au}_{10}\text{Cl}_3(\text{Pcy}_2\text{Ph})_6]^+$ and $[\text{Au}_{10}(\text{PPh}_3)_7\{\text{S}_2\text{C}_2(\text{CN})_2\}_2]$ have different total numbers of valence electrons their skeletal geometries are identical because they both have $[\text{Au}_{10}]^{4+}$ cores. The electronic factors enabling gold clusters to maintain the same skeletal geometry when additional terminal ligands are coordinated have been

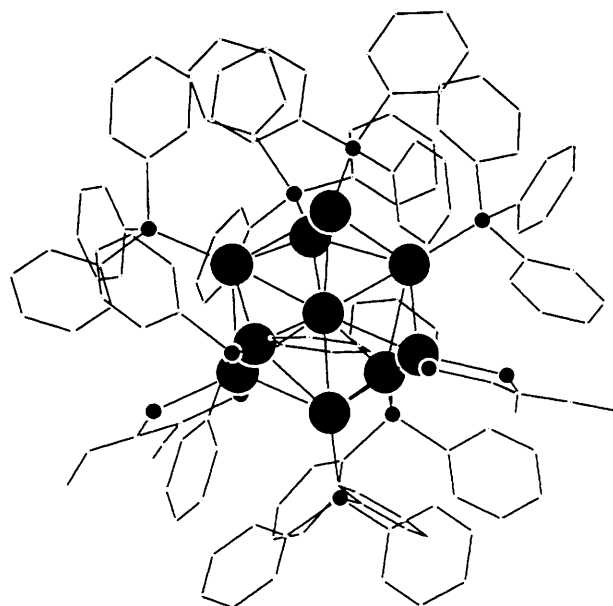


Fig. 1 Structure determined for $[\text{Au}_{10}(\text{PPh}_3)_7\{\text{S}_2\text{C}_2(\text{CN})_2\}_2]$ drawn by PLUTO.¹⁵ Au–Au bond lengths are in the range 2.567(4)–3.055(4) Å; Au–P bond lengths are in the range 2.20(2)–2.36(2) Å; Au–S bond lengths are in the range 2.26(2)–2.50(2) Å.

[†] Microanalysis (performed by Mr M. Gascoyne, Inorganic Chemistry Laboratory, Oxford) gave satisfactory results for C, H, Au and N analysis.

[‡] Crystal data: $\text{C}_{134}\text{H}_{105}\text{Au}_{10}\text{N}_4\text{P}_7\text{S}_4$, $M = 4086.10$, monoclinic, $a = 52.74(4)$, $b = 16.65(1)$, $c = 30.40(1)$ Å, $\beta = 97.06(7)^\circ$, space group $C2/c$, $U = 26492.5 \text{ \AA}^3$, $F(000) = 15168$, $D_c = 2.05 \text{ g cm}^{-3}$, $Z = 8$, $\mu[\lambda = 0.895(5) \text{ \AA}] = 171.0 \text{ cm}^{-1}$.

Data collection and structure solution: SRS (Synchrotron Radiation Source, Daresbury Laboratory) workstation 9.6, wavelength 0.895(5) Å, FAST area detector diffractometer, 200° of data measured in 0.3° frames by rotating the crystal about the diffractometer z -axis, 10 s per frame, SRS at 2 GeV, 273 mA, total data collection time ca. 2 h. The data were processed off-line using MADNES¹⁰ software with modifications for synchrotron radiation work,¹¹ in a manner similar to that described by Rizkallah, Maginn and Harding.¹² This gave unit cell parameters and then intensities of 15391 reflections (MADNES flag 0 and 1), 6470 unique, $R_{\text{merge}} = 0.038$. Weighted, full-matrix least-squares refinement (SHELX¹³), with phenyl rings constrained as regular hexagons, anisotropic vibration parameters for Au and S, isotropic for all others (no hydrogen atoms included), gave $R = 0.064$ and $R_w = 0.065$ for 3747 unique reflections with $F > 6\sigma(F)$; $w = 1/[\sigma^2(F) + gF^2]$ where $g = 0$ after a DIFABS¹⁴ absorption correction had been applied; S (goodness of fit) = 1.015, residual electron density $+0.55$, -0.71 e \AA^{-3} . Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

discussed in detail elsewhere.⁹ The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at room temperature shows only one broad resonance at δ 47.9. At 230 K four signals are revealed at δ 55.6, 53.4, 43.4 and 40.7 in a ratio 2:1:2:2. This is consistent with the structure found in the solid state.

The transformation of $[\text{Au}_8(\text{PPh}_3)_7][\text{S}_2\text{C}_2(\text{CN})_2]$ into $[\text{Au}_{10}(\text{PPh}_3)_7\{\text{S}_2\text{C}_2(\text{CN})_2\}_2]$ under such mild conditions would certainly not have been detected without the single crystal data above, and the successful solution of the structure from such small crystals opens up an approach to many characterisation problems in this area of cluster chemistry.

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