Preparation and Properties of Gold Atom Cluster Compounds: Octakis-(triarylphosphine)enneagold Trianion

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A new series of gold cluster compounds has been identified. These are tri-univalent electrolytes, with the general formula $(Au_9L_8)X_3$ [L = PPh_3 or $P(C_6H_4Me\text{-}p)_3$, and X = NO_3, PF_6, picrate, BF_4, or ClO_4].

We have previously reported[1] gold cluster compounds with the general formula: $Au_{11}X_3L_7$ [X = CN, SCN, or I and L = PPh_3 or $P(C_6H_4X\text{-}p)_3$], structures for these have been reported by other workers.[2,3] The cluster compounds $Au_{11}X_3L_7$, were obtained by treating compounds of the type AuXL with $NaBH_4$, where X is an anionic ligand with strong co-ordinating properties. When X had poor ligand properties (*e.g.* NO_3) we isolated the compound $(Au_9L_8)(NO_3)_3$; by metathesis, we obtained the corresponding hexafluorophosphate, picrate, tetrafluoroborate, and perchlorate derivatives.

The preliminary results of the *X*-ray structural investigation on the hexafluorophosphate derivative with the *p*-tolylphosphine ligand has confirmed the presence of an Au_9L_8 cage, as has been reported for the picrate and nitrate derivatives.[4]

Analytical data [a]

	Au	C	H	N	M.p.[b]	Λ_M[c]
$[Au_9\{PPh_3\}_8](NO_3)_3$	43·8 (43·7)	41·5 (42·6)	2·7 (2·9)	1·0 (1·0)	230	*d*
$[Au_9\{P(C_6H_4Me)_3\}_8](NO_3)_3$	40·1 (40·4)	45·8 (45·9)	3·8 (3·8)	0·9 (0·9)	257	*d*
$[Au_9\{PPh_3\}_8](PF_6)_3$	41·3 (41·2)	40·0 (40·1)	2·7 (2·7)		240	106
$[Au_9\{P(C_6H_4Me)_3\}_8](PF_6)_3$	37·8 (38·1)	43·4 (43·4)	3·3 (3·6)		280	100
$[Au_9\{(PPh_3)\}_8][C_6H_2O(NO_2)_3]_3$	39·0 (38·9)	42·1 (42·5)	2·6 (2·7)	2·3 (2·7)	170	81
$[Au_9\{(PPh_3)\}_8](BF_4)_3$	43·6 (43·0)	41·8 (41·85)	2·9 (2·9)		240	*d*
$[Au_9\{(PPh_3)\}_8](ClO_4)_3$	42·8 (42·6)	40·4 (41·5)	2·8 (2·8)		238	97

[a] Theoretical values in parentheses. [b] Decomp., °C. [c] Molar conductance (Ω^{-1} cm^2 ml^{-1}) of 10^{-3}M solutions in nitrobenzene. [d] Insoluble.

The compounds show the typical i.r. spectra of non-co-ordinated anions, thus confirming their ionic nature.

The conductivity values in nitrobenzene solution at 25 °C for the hexafluorophosphate, perchlorate, picrate, and nitrate derivatives are in agreement with the ones calculated for tri-univalent electrolytes (Table).

The ^1H n.m.r. spectrum carried out on a solution of the picrate derivative in CD_2Cl_2, shows a singlet at τ 1·36, assigned to the two hydrogen atoms of the picrate anion, and a multiplet centred at τ 3·1, assigned to the hydrogens of the triphenylphosphine. The complexity of the latter signal is due to the non-equivalence of the eight phosphine molecules in the cluster. The ratio of the signal areas of the triphenylphosphine and the picrate is *ca.* 20, in agreement with the formula (Au_9L_8)-(picrate)$_3$.

A further confirmation of the phosphine : anion ratio was obtained from the ^{31}P n.m.r. analysis, carried out on a solution of the hexafluorophosphate derivative $[Au_9(PPh_3)_8](PF_6)_3$ in CH_2Cl_2. Such a spectrum shows for the anion PF_6 a septuplet centred at +58·49 p.p.m. with respect to H_3PO_4 (J_{PF} 713 Hz), and a signal for the phosphorus which is broad because of coupling of the phosphorus with the phenyl protons. This signal sharpens however upon proton-noise decoupling radiation. By this device one can have a sharp signal at −23·13 p.p.m. with respect to H_3PO_4. Since, the signals are relatively weak, the integration is not very accurate. In order to overcome this, ten integrals were run of the central peak of the septet and of the undecoupled triphenylphosphine peak. Using average values an intensity ratio of 4·38 : 38·4 was calculated. Taking account of the 1 : 6 : 15 : 20 : 15 : 6 : 1 binomial distribution in PF_6^-, this gives a ratio of 14·016 : 38·4 = 0·365 for the two types of P atoms in good agreement with the ratio 3 : 8 = 0·375 calculated for the formula $[Au_9(PPh_3)_8](PF_6)_3$.

EXPERIMENTAL

Gold analyses were carried out by decomposition of the complexes with sulphuric and nitric acids and subsequent dilution. Metallic gold separates and can be determined by filtration and weighing. C, H, and N were determined using a Perkin-Elmer 240 apparatus and the results are reported in the Table. Molecular weights were determined using a Mechrolab 302 Osmometer. Conductivity studies were made in nitrobenzene solution at 25 °C using a Phillips PR 9500 conductance bridge.

M.p.s were determined in an Electrothermal melting point apparatus and are uncorrected. I.r. spectra were recorded for KBr discs using a Perkin-Elmer model 621 spectrometer (Table).

The magnetic susceptibilities were determined at room temperature using a Gouy balance and all the compounds were found to be diamagnetic.

The ^1H n.m.r. spectra were recorded for CD_2Cl_2 solutions on a Varian HA 100 instrument, using tetramethylsilane

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[1] F. Cariati and L. Naldini, *Inorg. Chim. Acta*, 1971, **5**, 172.

[2] M. McPartlin, R. Mason, and L. Malatesta, *Chem. Comm.*, 1969, 334.

[3] V. G. Albano, P. L. Bellon, M. Manassero, and M. Sansoni, *Chem. Comm.*, 1970, 1210.

[4] P. L. Bellon, F. Cariati, M. Manassero, L. Naldini, and M. Sansoni, *Chem. Comm.*, 1971, 1423.

as internal reference. The ^{31}P n.m.r. spectra were recorded on a Varian XL 100 apparatus, in CH_2Cl_2 in an 8 mm tube, which was centred in a 12 mm tube containing D_2O and 20% H_3PO_4 as reference.

Octakis(triphenylphosphine)enneagold Trinitrate, $[Au_9(PPh_3)_8](NO_3)_3$.—To a suspension of $[PPh_3AuNO_3]$ (10 g, 19·2 mmol), in ethanol (350 ml) was added dropwise with stirring $NaBH_4$ (0·175 g, 4·6 mmol) in ethanol (100 ml). When the addition of $NaBH_4$ was complete a green crystalline compound began to separate; this was completed by addition of hexane. The compound was recrystallized from methylene chloride by addition of hexane. It was soluble in methylene chloride, fairly soluble in ethanol, slightly soluble in chloroform, benzene, and nitrobenzene.

*Octakis(tri-*p*-tolylphosphine)enneagold Trinitrate*, $[Au_9\{P(C_6H_4Me)_3\}_8](NO_3)_3$.—This compound was prepared from $[P(C_6H_4Me)_3AuNO_3]$ (5·66 g, 10 mmol) and $NaBH_4$ (0·09 g, 2·5 mmol) in a similar procedure to that described above. It was crystallized from methylene chloride–hexane.

Octakis(triphenylphosphine)enneagold Tris(hexafluorophosphate), $[Au_9(PPh_3)_8](PF_6)_3$.—To a solution of $[Au_9(PPh_3)_8](NO_3)_3$ (2 g, 0·5 mmol) in ethanol (250 ml) was added NH_4PF_6 (0·2 g, 1·4 mmol) dissolved in ethanol (100 ml). There was immediate formation of an insoluble pale green precipitate, which was crystallized from CH_2Cl_2–ethanol.

*Octakis(tri-*p*-tolylphosphine)enneagold Tris(hexafluorophosphate)*, $[Au_9\{P(C_6H_4Me)_3\}_8](PF_6)_3$.—This compound was prepared from $[Au_9\{P(C_6H_4Me)_3\}_8](NO_3)_3$ (3·3 g, 0·75 mmol) and NH_4PF_6 (0·3 g, 2·1 mmol) in a similar procedure to that described above. It was crystallized from CH_2Cl_2–hexane.

Octakis(triphenylphosphine)enneagold Tripicrate, $[Au_9(PPh_3)_8](Picrate)_3$.—This compound was prepared from $[Au_9(PPh_3)_8](NO_3)_3$ (2 g, 0·5 mmol) and picric acid (1 g, 4 mmol) in a procedure similar to that described above. It was crystallized from CH_2Cl_2–ethanol.

Octakis(triphenylphosphine)enneagold Tris(tetrafluoroborate), $[Au_9(PPh_3)_8](BF_4)_3$.—This compound was prepared from $[Au_9(PPh_3)_8](NO_3)$ (0·37 g, 0·09 mmol) and solution of HBF_4 (40%, 5 drops). It was crystallized from CH_2Cl_2–ethanol.

Octakis(triphenylphosphine)enneagold Tris(perchlorate), $[Au_9(PPh_3)_8](ClO_4)_3$.—This compound was prepared from $[Au_9(PPh_3)_8](NO_3)_3$ (1 g, 0·25 mmol) and $LiClO_4$ in ethanol solution. It was crystallized from CH_2Cl_2–ethanol.

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