Reactions of Gold–Phosphine Cluster Compounds

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Summary $[Au_9L_8]^{3+}$ ($L = PPh_3$) reacts with L to give $[Au_9L_{10}]^{3+}$ and with X^- (X = Cl, Br, I, CN, or SCN) to give $Au_9L_8X_3$ which converts into $[Au_{11}L_8X_2]^+$ in solution (investigated for X = Cl and SCN); from ^{31}P [^1H] n.m.r., i.r., and Mössbauer spectra it is concluded that these new Au_9 and Au_{11} clusters are structurally related to the known complexes $[Au_9L_8]^{3+}$ and $Au_{11}L_7X_3$, respectively.

THE $[Au_9L_8]^{3+}$ ion (L = PPh_3) reacts with L and (pseudo) halides X^- (X = Cl, Br, I, SCN, or CN) yielding other Au_9 and Au_{11} clusters; the reactions and the properties of the products are reported in this communication.

The reaction of PPh_3 (L) with $[Au_9L_8]^{3+}$-nitrate or -hexafluorophosphate in methylene chloride results in the formation of $[Au_9L_{10}]^{3+}$ which can be precipitated as its nitrate or hexafluorophosphate by addition of toluene. When $AuLNO_3$ is added to a solution of $[Au_9L_{10}]^{3+}$ the reverse reaction occurs, $[Au_9L_8]^{3+}$ and $[AuL_2]^+$ being the only products. These reactions were studied by measuring the proton-decoupled ^{31}P n.m.r. spectra for different amounts of L (or $AuLNO_3$) added to the solution. Chemical analysis confirmed the formation of $[Au_9L_{10}]^{3+}$.

Methanolic solutions of $Au_9L_8(NO_3)_3$ react with alkali metal salts of Cl^-, Br^-, I^-, SCN^-, and CN^-. At −50 °C $Au_9L_8X_3$ is precipitated as a pure compound on addition of water. From ^{31}P [^1H] n.m.r. measurements it can be concluded that at room temperature $Au_9L_8(SCN)_3$, dissolved in methanol, decomposes within 12 h and $[Au_{11}L_8(SCN)_2]^+$ is formed. In methylene chloride solution all $Au_9L_8(SCN)_3$ is converted into $[Au_{11}L_8(SCN)_2]^+$ within 15 min. Compounds $[Au_{11}L_8(SCN)_2](PF_6)$ and $[Au_{11}L_8Cl_2](PF_6)$ were prepared in methylene chloride by treating $Au_9L_8(NO_3)_3$ with 2 equiv. of $Bu_4N(SCN)$ and an excess of Bu_4NCl, respectively. After evaporation of the solvent and dissolving the residues in ethanol, precipitation was achieved through addition of NH_4PF_6. $[Au_{11}L_8Cl_2](PF_6)$ does not react with an excess of Cl^- in contrast with $[Au_{11}L_8(SCN)_2]$-(PF_6) which is converted into the well known compounds $Au_{11}L_7(SCN)_3$ by an excess of SCN^-.

Some of the properties and the preliminary *X*-ray structure results of $[Au_9L_8]^{3+}$ have been reported.[1] The structure of the Au-P skeleton is given in the Figure. The Mössbauer spectrum shows only one quadrupole pair with natural linewidth. The isomer shift (I.S.) and the quadrupole splitting (Q.S.) are similar to those of the peripheral phosphine-co-ordinated gold atoms in $Au_{11}L_7X_3$[2] (Table). No separate resonance line due to the central gold atom could be detected, in contrast with $Au_{11}L_7X_3$ where a singlet could be assigned to the central gold atom.[2]

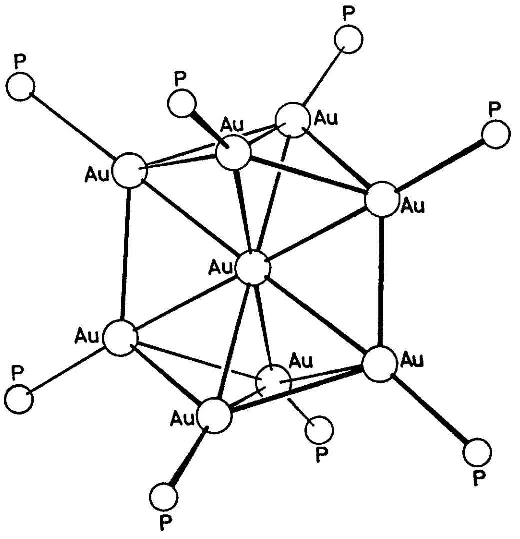

FIGURE. Au–P skeleton in $[Au_9L_8]^{3+}$.

The ^{31}P [^1H] n.m.r. spectra of methylene chloride solutions of $[Au_9L_8]^{3+}$ and $Au_{11}L_7X_3$ show only one singlet even at −90 °C; no rapid exchange with free L in solution is observed. The crystal structures of $[Au_9L_8]^{3+}$ [1] and $Au_{11}L_7X_3$[3] show two and three different Au–L sites, respectively. The simplicity of the ^{31}P [^1H] n.m.r. spectra is either due to shift differences too small to be detected or due to fast intramolecular processes interconverting these sites.

The Mössbauer spectrum of $[Au_9L_{10}]^{3+}$ shows one singlet and one quadrupole pair. The quadrupole pair has the same I.S. and Q.S. as the spectrum of $[Au_9L_8]^{3+}$ (see Table) and is therefore assigned to the eight peripheral gold atoms. The singlet then must be due to the central gold atom.

The ^{31}P [^1H] n.m.r. spectrum consists of two singlets with an intensity ratio 4 : 1. The low intensity line shows rapid exchange with free L in the methylene chloride solution.

TABLE 1. Mössbauer and ^{31}P [^1H] n.m.r. data of gold–phosphine clusters.

Complex		Mössbauer parameters/mm s^{-1} [a]			^{31}P [^1H] N.m.r.(δ/p.p.m.)[b]
		Au–L	Au–X	Au (central)	
$Au_9L_8(PF_6)_3$	I.S.	2·1	—	Not observed	−54·8 (CD_2Cl_2)
	Q.S.	6·6	—		
$Au_9L_{10}(PF_6)_3$	I.S.	1·9	—	2·6	−53·0 (peripheral Au–L)
	Q.S.	6·7	—	0	−43·6 (central Au–L)(CD_2Cl_2)
$Au_9L_8(SCN)_3$	I.S.	1·9	—	2·4	−53·0 (CD_2Cl_2; fast decomposition)
	Q.S.	6·8	—	0	−53·3 (CD_3OD; slow decomposition)
$Au_9L_8(CN)_3$	I.S.	1·9	—	2·4	Not measured
	Q.S.	6·8	—	0	
$Au_9L_8I_3$	I.S.	1·9	—	2·5	Not measured
	Q.S.	6·7	—	0	
$Au_9L_8Br_3$	I.S.	1·9	—	2·3	Not measured
	Q.S.	6·7	—	0	
$Au_{11}L_8(SCN)_2(PF_6)$	I.S.	1·5	0·5	2·7	−50·7 (CD_2Cl_2)
	Q.S.	6.6	4·6	0	
$Au_{11}L_8Cl_2(PF_6)$	I.S.	1·5	0·6	2·5	−50·2 (CD_2Cl_2)
	Q.S.	6·7	3·9	0	
$Au_{11}L_7(SCN)_3$[c]	I.S.	1·4	0·6	2·7	−49·9 (CD_2Cl_2)
	Q.S.	6·7	4·5	0	

[a] I.S. relative to ^{197}Pt-source. [b] Relative to $O{=}P(OMe)_3$ internal reference; all singlets apart from the septet of PF_6. [c] Mössbauer data are based on 5-line 3-sites interpretation (2 quadrupole pairs and 1 singlet); a 9-line 5-sites interpretation was given elsewhere (ref. 2).

The Mössbauer and ^{31}P [^{1}H] n.m.r. spectra of $[Au_9L_{10}]^{3+}$ can be explained by assuming that the gold skeleton in this complex is similar to that in $[Au_9L_8]^{3+}$ with the two extra phosphines bonded to the central gold atom. This atom is then 10-co-ordinated like the central gold atom in the Au_{11} clusters. The two added phosphines are rather weakly bonded and exchange rapidly with the free phosphine in the solution. Upon addition of a phosphine scavenger like $AuLNO_3$, $[Au_9L_8]^{3+}$ is rapidly recovered.

The Mössbauer spectrum of $Au_9L_8X_3$ is similar to that of $[Au_9L_{10}]^{3+}$ containing the quadrupole pair characteristic for peripheral Au–L and a singlet for the central gold atom (Table). Therefore we assume the gold skeleton to be the same as in $[Au_9L_{10}]^{3+}$.

The i.r. spectrum of $Au_9L_8(SCN)_3$ shows two SCN vibrations at 2050 and 2100 cm^{-1} pointing to free SCN$^-$ together with *S*-co-ordinated SCN. The i.r. spectrum of $Au_9L_8(CN)_3$ has one ν(CN) at 2120 cm^{-1} revealing that only co-ordinated CN is present.

The Mössbauer spectra of $[Au_{11}L_8(SCN)_2]^+$ and $[Au_{11}L_8Cl_2]^+$ show two quadrupole pairs characteristic for peripheral Au–L and Au–X sites, and a singlet due to a central gold atom (see Table).[2] The spectra differ from that of $Au_{11}L_7(SCN)_3$ only in the intensity ratio of the two quadrupole pairs, according to the different ratio of the L and X ligands.

The i.r. spectrum of $[Au_{11}L_8(SCN)_2](PF_6)$ shows only one SCN vibration at 2100 cm^{-1} pointing to *S*-co-ordinated SCN. Both $[Au_{11}L_8X_2](PF_6)$ compounds (X = Cl or SCN) are 1:1 electrolytes in Me_2SO solution. The ^{31}P [^{1}H] n.m.r. spectra show, like the other Au_{11} clusters, one singlet. We believe their structures to be closely related to that of $Au_{11}L_7X_3$ with 8 peripheral gold atoms bonded to L and 2 to SCN and Cl, respectively.

The reactivity of $[Au_9L_8]^{3+}$ discussed above seems to be caused by the exposed co-ordinatively unsaturated central gold atom. In this respect it is interesting to mention that all compounds reported here are red in solution as well as in the solid state with the notable exception of solid $[Au_9L_8]^{3+}$-nitrate or -hexafluorophosphate which is green. Details of the Au_9 into Au_{11} conversion are currently being investigated.

Satisfactory elemental analyses were obtained for all compounds reported.

The Mössbauer spectra were recorded at 4·2 K with apparatus described elsewhere.[4] The ^{31}P [^{1}H] n.m.r. spectra were recorded on a Varian XL-100-FT spectrometer at 40·5 MHz using the deuteriated solvent as an internal lock.

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