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Trianionoeptakis(triarylphosphine)undecagold Cluster Compounds

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Received, October 16, 1970

We report on the preparation of compounds of general formula $Au_{11}L_7X_3$ *(L = tris-*parasubstituted*phenylphophine, X = I⁻, SCN⁻, CN⁻) containing metal-metal bonds.*

Introduction

We previously reported the preparation of gold cluster compounds.[1-4] We have now isolated the following compounds, of general formula $Au_{11}L_7X_3$:

1) $Au_{11}[P(C_6H_4Cl)_3]_7I_3$
2) $Au_{11}[P(C_6H_4Cl)_3]_7(SCN)_3$
3) $Au_{11}[P(C_6H_4Cl)_3]_7(CN)_3$
4) $Au_{11}[P(C_6H_4CH_3)_3]_7(SCN)_3$
5) $Au_{11}[P(C_6H_4F)_3]_7(SCN)_3$
6) $Au_{11}[P(C_6H_4F)_3]_7I_3$

They are all prepared by treating the corresponding Au^I derivatives AuLX, with an ethanol solution of sodium tetrahydroborate. From the brownish precipitate thus obtained, we isolated the compounds as beautiful red crystals by fractional crystallization from methylene chloride or benzene with addition of ethanol or hexane.

Experimental Section

Gold analyses were carried out by decomposition of complexes with sulphuric and nitric acids and subsequent dilution. Metallic gold separates and can be determined by filtration and weight.

C and N were determined using a Perkin-Elmer 240 apparatus and the results are reported in Table I. Molecular weights were determined using a Mechrolab 302 Osmometer and are reported in Table II. Infrared spectra were recorded using a Perkin-Elmer model 621 spectrometer in the media indicated in Table III. The magnetic susceptibilities were determined at room temperature using a Gouy balance and all the compounds were found diamagnetic.

Triiodoeptakis[tri(4-chlorophenyl)phosphine]undecagold. 0.33 g (8.7×10^{-3} moles) of $NaBH_4$ are added, slowly with stirring, to 6 g (8.7×10^{-3} moles) of $AuP(C_6H_4Cl)_3I$ in 300 ml of ethanol and the mixture is stirred for 2 h.

The brown solution is treated with n-hexane and the precipitate obtained is fractionally crystallised by dissolution in methylene chloride, followed by filtration and addition of ethanol to give a red crystalline compound.

Trithiocyanoeptakis[tri(4-chlorophenyl)phosphine]-undecagold. 0.063 g (1.65×10^{-3} moles) of $NaBH_4$ are added, slowly with stirring, to 1.03 g (1.65×10^{-3} moles) of $AuP(C_6H_4Cl)SCN$ suspended in 150 ml of ethanol. On addition of n-hexane, a brown precipitate is obtained, which is fractionally recrystallised from benzene/n-hexane to give a red crystalline compound.

Tricyanoeptakis[tri(4-chlorophenyl)phosphine]undecagold. 0.340 g (8.91×10^{-3} moles) of $NaBH_4$ are added to 5.26 g (8.91×10^{-3} moles) of $AuP(C_6H_4Cl)CN$ suspended in 250 ml of ethanol with stirring. After 1 h the mixture is filtered and the solution evaporated to dryness, then methylene chloride is added and the mixture is filtered By fractional crystallization with ethanol red crystals are obtained.

Trithiocyanoeptakis[tri(4-tolyl)phosphine]undecagold. 0.294 g (7.55×10^{-3} moles) of $NaBH_4$ are added to 4.23 g (7.55×10^{-3} moles) of $AuP(C_6H_4CH_3)_3SCN$ suspended in 500 ml of ethanol with stirring. After three hours the mixture is filtered and the solution evaporated to dryness, then methylene chloride is added and the mixture filtered again. By fractional crystallization with n-hexane, a red crystalline compound is obtained from the solution.

Trithiocyanoeptakis[tri(4-fluorophenyl)phosphine]-undecagold. 0.254 g (6.7×10^{-3} moles) of $NaBH_4$ are added to 3.83 g ($6.7\times{}^{-3}$ moles) of $AuP(C_6H_4F)_3SCN$ suspended in 200 ml of ethanol with stirring. After two hours, addition of n-hexane causes a brown precipitate to separate. It is dissolved in methylene chloride and, by fractional crystallization with n-hexane, a red crystalline compound is obtained.

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(1) L Malatesta, L. Naldini, G. Simonetta, and F. Cariati, *Chem. Comm.*, 212 (1965).
(2) L. Malatesta, L. Naldini, G. Simonetta, and F. Cariati, *Coord. Chem. Rew.*, *1*, 255 (1966).
(3) F. Cariati, L. Naldini, G. Simonetta, and L. Malatesta, *Inorg. Chim. Acta*, *1*, 315 (1967).
(4) F. Cariati, L. Naldini, G Simonetta, and L. Malatesta, *Inorg. Chim. Acta*, *1*, 34, (1967).

Table I.

Compound [a]	C	H	Au	Cl	I, N
$Au_{11}[P(C_6H_4Cl)_3]_7I_3$	2.4.(29.6)	1.64(1.64)	42.5(42.5)	14.4(14.6)	7.45(7.49)
$Au_{11}[P(C_6H_4Cl)_3]_7(SCN)_3$	33.6(31.6)	2.08(1.71)	45.2(44.2)	14.5(15.2)	0.87(0.86)
$Au_{11}[P(C_6H_4Cl)_3]_7(CN)_3$	31.9(32.2)	1.74(1.75)	45.1(45.0)	15.05(15.5)	0.94(0.87)
$Au_{11}[P(C_6H_4CH_3)_3]_7(SCN)_3$	40.8(40.4)	2.93(3.28)	47.7(48.4)		0.97(0.94)
$Au_{11}[P(C_6H_4F)_3]_7I_3$	31.5(31.8)	1.55(1.76)	45.1(45.5)		7.8 (8.0)
$Au_{11}[P(C_6H_4F)_3]_7(SCN)_3$	33.04(33.8)	1.44(1.84)	46.5(47.5)		0.97(0.92)
$Au_{11}[P(C_6H_5)_3]_7(SCN)_3$	37.1(37.1)	2.58(2.52)	52.4(52.0)		1.16(1.0)
$Au_{11}[P(C_6H_5)_3]_7(CN)_3$	38.6(37.9)	2.72(2.57)	52.0(53.1)		1.12(1.03)
$Au_{11}[P(C_6H_5)_3]_7I_3$	34.3(34.5)	2.47(2.39)	46.5(49.4)		9.8 (8.68)

[a] The numbers in parentheses refer to theoretical values.

Table II.

Compound	m.w.calc.	m.w.found in $CHCl_3$	m.p. [d]
$A_{11}[P(C_6H_4Cl)_3]_7I_3$	5106	5260	192°
$A_{11}[P(C_6H_4Cl)_3]_7(SCN)_3$	4899	4720	208°
$A_{11}[P(C_6H_4Cl)_3]_7(CN)_3$	4803	5040	205°
$A_{11}[P(C_6H_4CH_3)_3]_7(SCN)_3$	4469	4200	189°
$A_{11}[P(C_6H_4F)_3]_7I_3$	4760	—	215°
$A_{11}[P(C_6H_4F)_3]_7(SCN)_3$	4553	5000	213°
$A_{11}[P(C_6H_5)_3]_7(SCN)_3$	4175	4500	180°
$A_{11}[P(C_6H_5)_3]_7(CN)_3$	4079	—	173°
$A_{11}[P(C_6H_5)_3]_7I_3$	4381	—	146°

[d] with decomposition.

Table III. C-N stretching frequencies (cm^{-1}) [a]

Compound	Nujol	$CHCl_3$	C_6H_6
$Au_{11}[P(C_6H_4Cl)_3]_7(SCN)_3$	2104.5	2104.5	2107.8
$Au_{11}[P(C_6H_4Cl)_3]_7(CN)_3$	2116.2	2118.6	2118
$Au_{11}[P(C_6H_4CH_3)_3]_7(SCN)_3$	2100.2	2099	2101
$Au_{11}[P(C_6H_4F)_3]_7(SCN)_3$	2128 m 2110 v s 2060 w	2107	2110
$Au_{11}[P(C_6H_5)_3]_7(SCN)_3$	2102	2102	2102.4
$Au_{11}[P(C_6H_5)_3]_7(CN)_3$	2119	—	—

[a] All bands are strong unless otherwise stated.

Triiodoeptakis[tri(4-fluorophenyl)phosphine]undecagold. 0.079 g (2.06×10^{-3} moles) of $NaBH_4$ are added to 1.315 g (2.06×10^{-3} moles) of $AuP(C_6H_4F)_3I$ in 150 ml of ethanol with stirring. After one hour, addition of n-hexane causes a brown precipitate to separate. It is dissolved in methylene chloride and, by fractional crystallization with ethanol, a red crystalline compound is obtained.

Trithiocyanoeptakis(triphenylphosphine)undecagold. 0.128 g (3.37×10^{-3} moles) of $NaBH_4$ are slowly added to 1.75 g (3.37×10^{-3} moles) of $AuP(C_6H_5)_3SCN$ in 150 ml of ethanol with stirring. After one hour, addition of n-hexane causes a brown precipitate to separate. This is dissolved in benzene and by fractional crystallization with ethanol a red crystalline compound is obtained.

Tricyanoeptakis(triphenylphosphine)undecagold. 0.344 g (9×10^{-3} moles) of $NaBH_4$ are added to 4.4 g (9×10^{-3} moles) of $AuP(C_6H_5)_3CN$ in 270 ml of ethanol with stirring. After one hour, the mixture is filtered and the red precipitate is washed with methylene chloride, ethanol, water and finally with ethanol again.

Results and Discussion

The analytical results, though quite satisfactory for the above formulations, would not have been sufficient by themselves to characterize these compounds. However, their structures have been solved and partially refined by the Molecular Structure Study Group of this Institute.[5] These results have confirmed for $Au_{11}[P(C_6H_4Cl)_3]_7I_3$ the stoichiometry and have assigned to the molecule a C_3 symmetry. One of the gold atoms is surrounded by the other ten metal atoms, seven of which are bound to a phosphine ligand and three to an iodide ion (see Figure 1). Crystallographic analysis is being carried out on the remaining compounds and the preliminary results show that the same molecular pattern is present by all of them.[5]

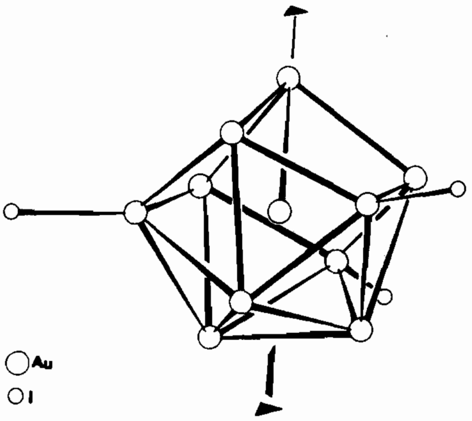

Figure 1. Perspective view of the $Au_{11}I_3$ group.

It ought to be noted that all the above mentioned clusters have a constant number of anionic ligands, namely three.

What appears really interesting to us is the fact that the presence of some gold atoms with positive oxidation number seems to be required for the formation of the cluster, perhaps to lower the electron density of the cluster.

I.R. spectra (Table III) confirm the presence of the covalent bond between the cyanide or thiocyanide

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(5) V.G. Albano, P.L. Bellon, M. Manassero, and M. Sansoni, *Chem. Comm.*, 1210 (1970).

anions and the metal atoms. The number of the CN stretching frequencies is the same either in solution or in the solid state, showing that both states have the same geometric arrangement. According to group theory, for C_3 symmetry two I.R. active bands of the same intensity are expected for the CN stretching modes. Most of these clusters show only one band. This fact can be explained by considering that the dimensions of the cluster forbid vibrational interactions of the anionic groups, so that only a local symmetry has to be considered. Only the solid state IR spectrum of the compound $Au_{11}[P(C_6H_4F)_3]_7(SCN)_3$ shows three bands in the C–N stretching frequencies region. However, in solution only one band appears, hence we can suppose the other two are due to solid state molecular interactions.

We would like to emphasise that the small shifts of the CN stretching frequencies of these clusters, observed on changing the substituent in the para position of the aromatic ring, are the same of those shown by the corresponding monomeric compounds, *i.e.* AuLX.[7]

We previously prepared the compound $Au_{11}[P(C_6H_5)_3]_7(SCN)_3$, belonging to the same series, and its structure has already been determined.[6] Its preparation has not hitherto been described. It was obtained by an analogous method to that used for the cited compounds with parasubstituted phosphines. Similarly, the compounds we previously described as $Au_3[P(C_6H_5)_3]_2(CN)$ and $Au_3[P(C_6H_5)_3]_2I$[2] probably belong to the same series and hence are better formulated as $Au_{11}[P(C_6H_5)_3]_7(CN)_3$ and $Au_{11}[P(C_6H_5)_3]_7I_3$. The calculated elemental analysis of the two different formulas are very close and we were not able to choose between the two possible formulas. Also because of their very low solubility, we did not carry out any determination of molecular weight and were unable to obtain suitable crystals for X-ray analysis which could confirm the presence of a cluster consisting of eleven gold atoms for these two compounds.

Acknowledgments. This work has been financially supported by the National Research Council of Italy. The Authors acknowledge a number of helpful discussions with the collegues involved in X-ray studies in this Centre[5] and with Prof. L. Malatesta.

(6) M. McPartlin, R. Mason, and L. Malatesta, *Chem. Comm.*, 334 (1969).

(7) F Cariati, D. Galizzioli, and L. Naldini, *La Chimica e l'Industria*, 52 995 (1970).