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XPS Photoelectron Spectra of Cluster Compounds of Gold*

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The XPS photoelectron spectra of mononuclear and polynuclear gold compounds of general formula $Au_nL_mX_p$ *(L = unsubstituted and* para-*substituted triphenylphosphine, X = anionic ligand) have been measured. The interpretation of the photoelectron data gives structural information on some clusters of unknown structure and also information on bonding properties in polynuclear gold compounds.*

Introduction

Gold cluster compounds, obtained by reduction of LAuX (where L = $P(C_6H_5)_3$, $P(p\text{-}C_6H_4CH_3)_3$, $P(p\text{-}C_6H_4Cl)_3$, $P(p\text{-}C_6H_4F)_3$ and X is an anionic ligand) with sodium borohydride, potassium hydroxide in alcohol, have been known for some time [1]. The structures of several of these compounds have been resolved by X-ray crystallography, which shows that they may be classified into the following three types:

(a) $[Au_{11}L_7X_3]$
(b) $[Au_9L_8]X_3$
(c) $[Au_6L_6]X_2$.

Compounds of type (a) are obtained by reduction of LAuX, when X = I^-, CN^-, SCN^-, while those of type (b) are obtained when X has very poor coordinating properties, *e.g.* NO_3^-, PF_6^-. Compounds of type (c) are obtained only when X = $[B(C_6H_5)_4]^-$, and the reaction conditions are not yet entirely clarified. The cluster present in the latter is a hexameric cation having a centrosymmetric, slightly distorted, octahedral structure [2, 3].

The structure of the 11 gold atoms cluster, Au_{11}, present in compounds of type (a), has been interpreted in two ways: either as a pentagonal bipyramid [4], sharing an apex with a tetragonal pyramid, or as a structure derived from an icosahedron in which there is a single atom at the centre of the face, instead of three atoms at the apexes of the triangular face [5]. In the first interpretation the central atom is considered to be Au^0, three of the remaining ten atoms being Au^I and the other seven Au^0. In the second interpretation [5], besides the previous interpretation [2], the authors also suggested the possibility of a central Au^{III} with ten peripheral Au^0.

The coordination polyhedron of 9 gold atoms, Au_9, present in compounds of type (b) may be considered to be a centred icosahedron lacking an equatorial rectangle [6]. In this structure the central gold atom is bonded to eight peripheral gold atoms, each of which is, in turn, bonded to a single ligand L.

Apart from these compounds of known structure, the compound $[Au_{11}L_9Cl]Cl_2$ has been identified from elemental analysis and from its metathetical reaction with compounds of type NaY, where Y = ClO_4^-, PF_6^-, NO_3^-, $[B(C_6H_5)_6]^-$ [1c]. In fact, this reaction gives compounds having molar conductivity characteristic of uni–bivalent compounds.

The crystal structures of many other polynuclear gold compounds could not be determined because they are given only as polycrystalline powder, and further characterization was often impossible because of the low solubility and instability in the common organic solvents. Having rationalised XPS (ESCA) data on clusters of known structure, we attempt an application of the photoelectron spectroscopy diagnostically to clusters of unknown structure. The aim is to assign formal oxidation state(s) to the gold atoms and obtain further information on the chemical bond in this interesting class of compounds. For reference purposes, the spectra of mononuclear gold compounds with differently substituted phosphines and having several anionic ligands (the same as

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those present in the clusters), in which the metal atom is present in different oxidation states and different coordination types, have been examined.

Experimental

XPS photoelectron spectra were recorded with a VG ESCA 3 spectrometer. The X-ray source was the $AlK_{\alpha 1,2}$ (1486.6 eV) line. The pressure in the analyser chamber was between 10^{-8}–10^{-9} torr.

Compounds were prepared by literature methods [1]. The spectra were registered on products deposited from alcohol suspension onto steel sample plate. This technique was used in order to obtain a thin homogeneous film of compound so as to avoid surface charging effects. The Au4f, P2p, and C1s binding energies were scanned. The C1s binding energy of phosphines was taken as an internal reference (in this case it coincides with the carbon of the contamination vacuum system, referenced to the carbon 1s peak of graphite at 284.0 eV). The binding energies reported are measured at the half width of the half maximum of the band. The FWHM's of the gold 4f bands lie in the interval 1.4 eV (metallic gold) to 2.2 eV. Possible changes in products under the action of X-rays were monitored using repeated scans; when doubt existed spectra were also registered at liquid nitrogen temperature. Measurements of the average of three independent values on different samples, to compensate errors due to charging effects, are considered good to ±0.2 eV. When necessary, a DuPont 310 Curve Resolver was used for peak deconvolutions by use of a Gaussian shape fit.

Results and Discussion

The influence of the different types of phosphines L and of anions X on the formation of the type of clusters is not yet clear. In addition the gold atoms may have different coordination numbers and, according to some authors [5], different oxidation numbers. The XPS spectra of the mononuclear gold(I) and gold(III) compounds, differing in the nature and numbers of phosphines bonded to the metal and also in the anion present, have been measured. These data should allow correlation of the different cases with their effect on the gold and phosphorus core electron energies, providing a basis for discussion of the data for the polynuclear compounds.

Tables I–IV list the binding energies for the 4f electrons of gold and the 2p electrons of phosphorus together with their FWHM. Only the binding energies of the 7/2 component of the $4f_{7/2}$ and $4f_{5/2}$ gold doublet is reported. In all cases the separation 3.6 eV and the intensity of the doublet 8:6 (ratio of the component band areas) were checked. Together with the FWHM, these values ensure that the photoelectron band is associated with only one type of gold atom. The band of the P2p electrons comprises two components (3/2 and 1/2) separated by *ca.* 1 eV; given the spectrometer characteristics, this could not be resolved.

TABLE I. $Au4f_{7/2}$, P2p Binding Energies (eV) and FWHM (eV) for Gold(I) Mononuclear Compounds.

Compound	$Au4f_{7/2}$	FWIIM	P2p	FWHM
$L' = P(C_6H_5)_3$			130.3	2.4
$L'' = P(C_6H_4Cl)_3$			130.2	2.2
$L''' = P(C_6H_4CH_3)_3$			130.2	2.3
$[L'AuCl]$	84.5	1.7	131.4	2.4
$[L''AuCl]$	84.5	1.8	131.3	2.4
$[L'''AuCl]$	84.6	1.7	131.3	2.4

TABLE II. $Au4f_{7/2}$, P2p Binding Energies (eV) and FWHM (eV) for Gold(I) Mononuclear Compounds.

Compound	$Au4f_{7/2}$	FWHM	P2p	FWHM
$[L'AuNO_3]$	84.6	1.9	131.3	2.2
$[L'_2Au]NO_3$	84.6	1.9	131.0	2.1
$[L'_3Au]NO_3$	84.6	1.8	130.8	2.1
$[L'AuSCN]$	84.6	1.9	131.3	2.2
$[L'_2AuSCN]$	84.6	1.8	131.0	2.1
$[L'_3Au]SCN$	84.5	1.9	130.8	2.3
$[L'AuCl]$	84.5	1.7	131.4	2.4
$[L'_2AuCl]$	84.6	1.6	130.9	2.3
$L' = P(C_6H_5)_3$			130.3	2.4

TABLE III. $Au4f_{7/2}$ Binding Energies (eV) and FWHM (eV) for Different Oxidation States for the Metal.

Compound	$Au4f_{7/2}$	FWHM
Au	83.0	1.4
$[L'AuCl]$	84.5	1.7
$[L'AuCl_3]$	86.5	1.9

TABLE IV. $Au4f_{7/2}$, P2p Binding Energies (eV) and FWHM (eV) for Gold Cluster Compounds.

Compound	$Au4f_{7/2}$	FWHM	P2p	FWHM
$[Au_9L'_8](NO_3)_3$	84.4	2.0	131.3	2.4
$[Au_{11}L'_7(CN)_3]$	83.7	1.9	131.2	2.1
$[Au_{11}L'_7(SCN)_3]$	83.7	2.2	131.2	2.4
$[Au_{11}L'_9Cl]Cl_2$	83.8	2.2	130.8	2.4
$Au_nL''_mCl_p$	83.6	2.2	130.8	2.3
$Au_nL'''_mCl_p$	83.6	2.2	130.8	2.2

Para-substitution of the benzene rings of the triphenylphosphine has a negligeable influence on the P2p binding energy in both the free ligands and the mononuclear compounds (see Table I). The *para*-substitution also has negligeable effect on the metal atom nor is there any change with change in the anion (see Table II). Inspection of Table II shows that the P2p binding energies in the coordinated phosphine. This indicates strong sharing of the phosphorus lone pair in the Au–P bond, which lowers the electron density on the phosphorus atom. Table II also shows the effect of phosphorus atom. Table II also shows the effect of increasing coordination number of the gold with changing number of phosphines coordinated from 1 to 2 to 3. There is a decrease in the P2p binding energy, whilst that of the Au4f$_{7/2}$ remains constant, independently of the anion. This indicates a practically constant charge distribution on the metal with variation in coordination number, which can be attributed to the particularly stable configuration ($5d^{10}$) assumed by the gold in these compounds. Because of this, with increasing number of phosphines in the monomer, the excess of electron density donated *via* σ bonding from the phosphines to the gold is redistributed *via* back donation from the metal to the empty π orbitals of the phosphines. All the series of compounds L_nAuX (where X = NO_3^-, SCN^-, Cl^-) reported in Table II show a decrease in the P2p binding energy with increase of n, although this variation is rather small. Note that for a fixed coordination number these energy values do not depend on the anion X.

The data of Table III show variation in the 4f$_{7/2}$ binding energy as a function of the gold oxidation number in mononuclear compounds. The oxidation numbers examined are 0, I, III, *i.e.* those attributable to the gold atoms in the clusters. For the formal oxidation state 0, the binding energy of the metallic gold was used since mononuclear Au^0 phosphine complexes do not exist (the polynuclear compounds are obtained during attempts to prepare them). If the oxidation state is increased by one unit, the 4f$_{7/2}$ binding energy increases by 1 to 1.5 eV. This behaviour is expected, as it has been demonstrated [7] that the binding energies of the core electrons depend mainly on the charge density of the atom from which the electron is photoionised.

Table IV lists data on the gold polynuclear compounds. The structural data for the clusters Au_9 and Au_{11} show the presence of three and five atoms, respectively, of gold with different coordination [2–5]. Given the ionic radii present, presumably metal atoms with different charge density are present. The photoelectron spectra show a single (4f$_{7/2}$) gold band, similar in form to that present in the mononuclear compounds (the FWHM's, of *ca.* 2 eV, are also similar). This behaviour is shown in the Figure, which compares the Au4f doublet for a polynuclear compound, a mononuclear compound and metallic gold. The results do indicate the presence in the clusters of gold atoms having very similar charge density, which can be ascribed to a strong electron delocalization over the entire coordination polyhedron. From the Figure, a difference in the form of the minimum between the components of the 7/2 and 5/2 doublet is evident; the minimum is higher in intensity than in both the mononuclear compound and in metallic gold. This indicates the presence of gold atoms, with binding energy at *ca.* 85.5 eV, and then with a lower electron density than that present in the other atoms responsible for the principal band. Deconvolution of the 4f bands of $[Au_{11}L_7X_3]$ and $[Au_9L_8]X_3$ gives ratios of 10:1 and 8:1 for the areas between the principal doublet and that obtained by deconvolution, for the Au_{11} and Au_9 clusters, respectively. The Figure reports the deconvolution for $[Au_{11}L'_7(SCN)_3]$. This result supports the suggestion, based on the X-ray determinations, that the central atom of the cluster, associated with the band at higher binding energy, has an electron density lower than the other metal atoms and lying between that of Au^I and Au^{III}.

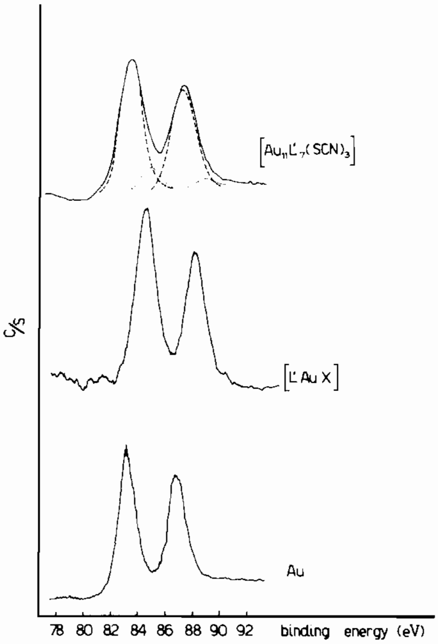

Figure. Photoelectron spectra (Au4f doublet) for a polynuclear gold compound, a mononuclear compound, and metallic gold.

The values of Table IV, which refer to the energy at half maximum of the band, indicate that the Au4f$_{7/2}$ binding energy lies between that of Au^0 and Au^I and it is greater in the Au_9 cluster than in the Au_{11} one. This agrees with an average oxidation number of 3/9 (Au_9) and 3/11 (Au_{11}) for the gold atoms. The P2p binding energy in the Au_9 cluster is the same as that in the LAuX monomer, which has practically the same Au/L ratio.

The last two clusters of Table IV were of unknown structure, due mainly to the impossibility of obtaining crystalline samples suitable for X-ray investigations. Elemental analyses were consistent with several formulae, which correspond to different oxidation numbers of the gold atoms. On the grounds of the $Au4f_{7/2}$ binding energies, reported in Table IV, average oxidation numbers on the metal greater than 3/9 and lower than 3/11 can be excluded. The latter value, however, seems to be most likely one and comparison of the phosphorus binding energies of Table IV indicates $Au_{11}L_9Cl_3$ as the most probable formula for these clusters. Thus, within the class of Au_{11} clusters, the phosphorus binding energy decreases with increasing number of the phosphines coordinated, as also found in the monomers (see Table II). Spectral deconvolution for clusters of type $[Au_{11}L_9Cl]Cl_2$ indicates the presence of a gold atom having a charge density lower than that of the other ten atoms; presumably that in the centre of the metal polyhedron.

This work shows that XPS photoelectron spectroscopy, being very sensitive to variations in atomic charges, is very useful for structural investigations on metal cluster compounds. However, diagnostic use for different coordination situations is not immediately evident. Nevertheless, analysis of the ligand binding energies can give information on the σ and π character of the Au–P bond and therefore, indirectly, information on coordination effects.

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