X-Ray Photoelectron Spectra of Some Gold Compounds

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The *X*-ray photoelectron spectra of a range of gold complexes with halide, phosphine, and thiol ligands is reported. Gold(I) and gold(III) complexes can readily be distinguished for each type of ligand. The use of this result is illustrated by following the decomposition of $[NEt_4][AuBr_4]$ on exposure to the *X*-ray beam. Systematic variations in the binding energies of the Cl 2*p*, Br 3*p*, P 2*p*, and S 2*p* levels have been observed between ligand, gold(I), and gold(III) complexes.

THE identification of the metal oxidation state and geometry of gold compounds is an important and, as yet, inadequately researched problem. For example, in studies of the role of gold in the treatment of rheumatoid arthritis, many of the model compounds prepared with ligands such as cysteine and penicillamine are of low solubility, non-crystalline, and often polymeric.[1-3] Standard techniques for identifying the oxidation state are less than definitive for gold. For example, gold(I) and gold(III) compounds are diamagnetic and their u.v.-visible spectra are difficult to interpret. Mössbauer spectroscopy has been used to identify gold oxidation states in individual and mixed-valence compounds and also to deduce some information on structure and bonding in these complexes.[4-7] These measurements require both liquid helium as a coolant and the use of an isotope of relatively short half-life. Another technique that can be applied is *X*-ray photoelectron (*X*-p.e.) spectroscopy. Extensive studies of the *X*-p.e. spectra of elemental gold and its alloys have been reported but studies of gold complexes have been concentrated mainly on gold ylide and gold cluster compounds.[8-10] Thus, it seemed of interest to extend these studies to include a wider range of gold(I) and gold(III) complexes.

TABLE 1

Binding energies (eV) of gold(I) and gold(III) halides

	Binding energies uncorrected for surface charging				Binding energies corrected by comparison with C_{1s} energy set at 285.3 eV					
Complex	Au $4f_{\frac{7}{2}}$	Cl 2*p*, Br 3*p*, I $3d_{\frac{5}{2}}$	Br 3*p*, I $3d_{\frac{3}{2}}$	C_{1s}	C_{1s}	Cl 2*p*, Br 3*p*, I $3d_2$	I $3d_{\frac{3}{2}}$	Au $4f_{\frac{7}{2}}$	f.w.h.m.	Trough depth
$[NEt_4][AuCl_2]$	84.7	198.5		284.9	285.3	198.9		85.1	1.6	81
	83.0	197.1		283.8	285.3	198.6		84.5	2.2	68
	81.9	195.8		282.5	285.3	198.6		84.7	1.7	84
$[NEt_4][AuBr_2]$	84.0	181.6	188.5	284.9	285.3	182.0	188.9	84.4	1.9	79
	83.6	181.6	188.2	284.7	285.3	182.2	188.8	84.2	1.9	77
$[NEt_4][AuI_2]$	85.9	621.4	632.4	287.0	285.3	619.7	630.7	84.2	1.9	75
	85.3	620.3	631.7	286.3	285.3	619.3	630.7	84.3	1.8	76
$[NEt_4][AuCl_4]$	87.1	198.5		284.6	285.3	199.2		87.8		
	86.2	197.8		284.2	285.3	198.9		87.3		
$[NEt_4][AuBr_4]$	87.4	183.5	190.1	286.0	285.3	182.8	189.4	86.7		
	86.2	181.8	188.5	284.5	285.3	182.6	189.3	87.0		
	86.1	181.8	188.6	284.9	285.3	182.2	189.0	86.5		
$[NEt_4][AuI_4]$	84.2	619.0	630.5	285.2	285.3	619.1	630.6	84.3	1.8	80

EXPERIMENTAL

Chlorogold(I) phosphine complexes[11] bis(triphenylphosphine)gold chloride,[12] tris(triphenylphosphine)gold nitrate, and tetrakis(triphenylphosphine)gold perchlorate,[13] the gold(I) and gold(III) halides,[14] and the gold(III) phosphine halide complexes[15] were prepared as described in the literature. Sodium gold thiomalate was obtained commercially.

Gold(I)–sulphur complexes were prepared as follows. To a stirred aqueous solution containing a three-fold excess of the ligand was added an aqueous solution of sodium tetrachloroaurate. The precipitate which formed was collected, washed with water and ethanol, then dried. In the case of penicillamine, a yellow precipitate formed initially which was filtered off. The filtrate was left to stand and a white precipitate slowly formed over a period of days. The latter precipitate was collected, washed, and dried as before.

Gold(III) penicillamine was prepared by the method of Brown *et al.*[4]

In all preparations, satisfactory microanalysis results were obtained.

The *X*-ray photoelectron spectra were recorded with a V.G ESCA 3 spectrometer. The *X*-ray source was the Al-K_α (1 486.6 eV) line and the working pressure was 10^{-6} Torr.† The samples were mounted on a probe, using double-sided Scotch tape. Throughout these experiments, the analyser resolution was kept constant.

RESULTS AND DISCUSSION

The magnitude of the surface charging effect experienced in this study is illustrated in Table 1. Throughout the rest of the study, all results are referred to the C_{1s}

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† Throughout this paper: 1 eV ≈ 1.60×10^{-19} J; 1 Torr = (101 325/760) Pa.

signals which were corrected to 285.3 eV for alkyl carbon and 284.9 eV for aryl carbon atoms, in agreement with previous work.[16] The alternative method of using a pump oil C_{1s} contamination peak as a standard was considered unsuitable, since it would take a considerable time to accumulate a suitable oil layer on the sample surface and, in view of the known reactivity of many gold complexes, this would be an undesirable procedure.

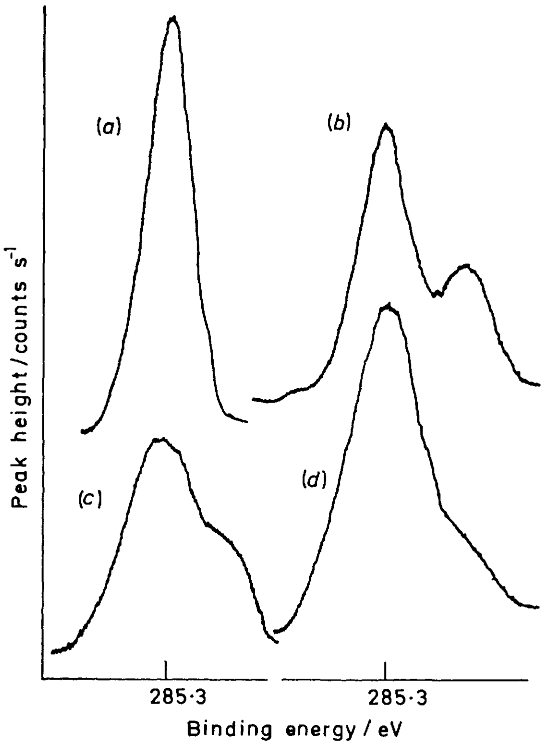

FIGURE 1 Carbon 1*s* binding energies for sulphur complexed to gold in (*a*) gold(I) octanethiol, (*b*) sodium gold thiomalate, (*c*) gold(I) cysteine, and (*d*) gold(III) penicillamine

With the majority of the compounds examined the C_{1s} signal was a singlet but, particularly with sulphur-containing ligands, splittings due to the different environments of the carbons were observed, as illustrated in Figure 1. The bands are assigned on the basis of their relative intensities. The lower binding-energy signal which, on the basis of intensity, is likely to be due to alkyl carbon atoms, was assigned the value 285.3 eV for calibration purposes. One spectrum, that of thiomalate, does not give rise to the expected intensity ratio for two carboxylate and two alkyl carbons. The full width at half-maximum (f.w.h.m.) and trough depths recorded do not, in comparison with the other spectra, suggest any decomposition and no time dependence of the signal was observed. The most likely explanation for this discrepancy is, therefore, that the signals from the carbon atoms on the carboxylate groups appear at different binding energies, with one of these signals remaining unresolved from the other C_{1s} signals.

Throughout this paper, f.w.h.m. and trough-depth values are given, both as an indication of the degree of resolution obtained and as a check on possible decomposition of the samples.

Tetraethylammonium Gold Halides.—Gold(I) halide complexes with tetraethylammonium cations all give very similar Au $4f_{\frac{7}{2}}$ binding energies, only *ca.* 0.5 eV higher than that found in metallic gold. The f.w.h.m. values are the smallest obtained in any series of complexes in this study and the signals do not change appreciably with time, so it seems likely that, in spite of the known reactivity of these species to water and other ligands and solvents, they remain stable to decomposition in the *X*-ray beam in the spectrometer. Tetra-alkylammonium tetrachloro- and tetrabromo-aurate(III), however, appear to react in vacuum in the *X*-ray beam over a period of 24—48 h. The result of one run is illustrated in Figure 2. In this case, the gradual appearance of a gold signal similar to that found for the gold(I) compounds and the gradual disappearance of the highest binding energy peak is apparent. It seems likely that the latter peak is a gold(III) signal from the original

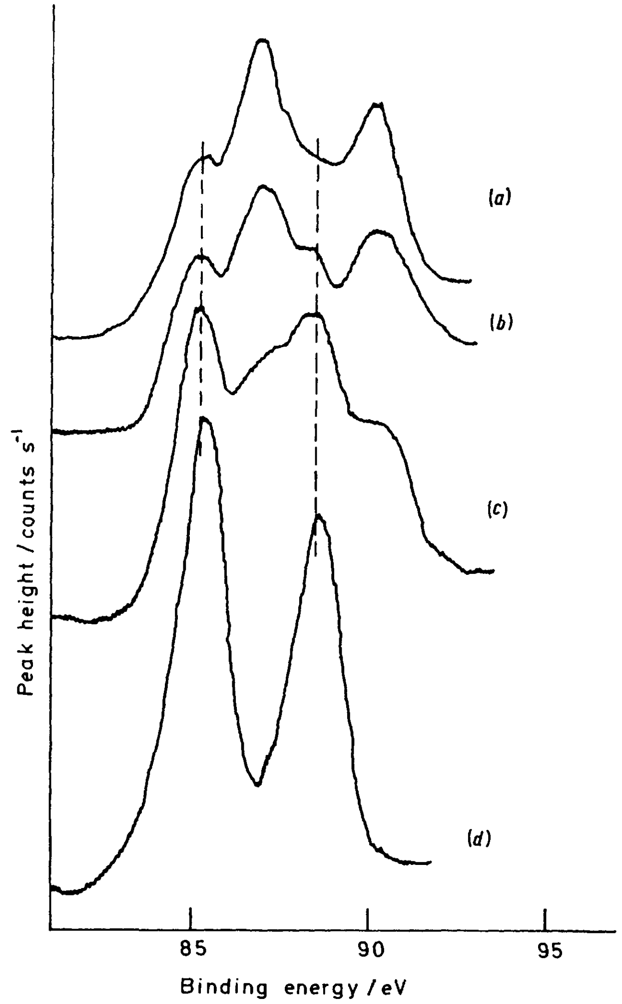

FIGURE 2 Decomposition in the *X*-ray beam of $[NEt_4][AuBr_4]$, after (*a*) 0.25 h, (*b*) 3 h, and (*c*) 24 h; (*d*) is the spectrum of $[NEt_4][AuBr_2]$. Arrowed peaks indicate those assigned to the disappearing gold(III) signal

compound and, consequently, this graph is an example of the use of *X*-p.e. spectroscopy to differentiate between gold(I) and gold(III).

A number of attempts to prepare tetraethylammonium tetraiodoaurate(III) were made. A crystalline compound which could be recrystallised from ethanol was prepared. No iodine could be leached out from it on washing with carbon tetrachloride. However, the empirical formula from analysis was consistent with $(C_2H_5)_4NAuI_{3.5}$ even after repeated recrystallisation. The p.e. spectrum indicated a gold(I) signal similar to that obtained for $[NEt_4][AuI_2]$. There is already some controversy concerning the AuI_4^- species, although its existence appears to be established in $K[AuI_4]$.[17] However, we observed no gold(III) signal and so the compound prepared here either decomposes at a faster rate than the bromide or chloride in the machine or, more likely, is indeed a gold(I) compound. Gold(III) results quoted in Table 1 were obtained by subtraction of the gold(I) signals. The spectrum of $K[AuCl_4]$ was also measured and, using the C_{1s} signal from the backing strip for calibration, a result in reasonable agreement with Schmidbaur *et al.*[9] and with the other results presented here was obtained.

TABLE 2

Binding energies (eV) of gold(I) phosphine complexes

Complex	C_{1s}	Cl $2p$	P $2p$	Au $4f_{\frac{7}{2}}$	f.w.h.m.	Trough depth
$[AuCl(PEt_3)]$	285.3	198.7	131.4	85.2	2.0	76
$[AuCl(PMePh_2)]$	285.0	198.8	n.d.	85.2	2.3	67
$[AuCl(PPh_3)]$	284.9	198.8	132.0	85.3	2.3	68
$[AuCl(PPh_3)_2]$	284.9	197.5	131.8	85.2	2.4	60
$[Au(NO_3)(PPh_3)_3]$	284.9		131.9	85.5	3.0	43
$[Au(ClO_4)(PPh_3)_4]$	284.9		131.0	85.0	3.0	42

n.d. = Not determined.

TABLE 3

Binding energies (eV) of gold(III) complexes of the type $[AuX_3L]$

Complex	C $1s$	P $2p$	Cl $2p$, Br $3p$	Au $4f_{\frac{7}{2}}$	f.w.h.m.	Trough depth
$[AuCl_3(PEt_3)]$	285.3	132.5	199.2	87.7	1.9	78
$[AuCl_3(PPh_3)]$	284.9	132.3	199.5	87.5	3.3	40
$[AuCl_3(py)]$	285.9		199.7	87.5	2.3	60
$[AuBr_3(PEt_3)]$	285.3	n.d.	182.6	87.1	2.7	50

py = Pyridine.

TABLE 4

Binding energies (eV) of gold complexes with thiols

Complex	C $1s$	S $2p$	Au $4f_{\frac{7}{2}}$	f.w.h.m.	Trough depth
Sodium gold(I) thiomalate	285.3	163.5	84.9	1.9	78
Gold(I) octanethiol	285.3	163.7	84.9	2.1	71
Gold(I) penicillamine hydrate	285.3	163.7	84.8	3.1	44
Gold(I) cysteine	285.3	163.4	84.5	2.5	55
Gold(I) glutathione	285.3	163.7	84.3	2.9	48
Gold(III) bis(penicillamine)	285.3	163.1	87.0	3.6	21

Phosphinegold Halide Complexes.—Changes in the phosphine ligand do not appear to affect the core binding energies of gold, chlorine, or phosphorus in compounds of type $[AuClL]$ where $L = PEt_3$, PPh_3, or $PMePh_2$. The average value of the Au $4f_{\frac{7}{2}}$ binding energy (85.2 eV) is rather lower than that found by Schmidbaur *et al.*[9] (85.55 eV) and Battistoni[8] (85.4 eV). The average Cl $2p$ and P $2p$ energies (198.8 and 131.6 eV, respectively) are similar to those found for related metal ions by Blackburn *et al.*,[16] who also noted that changing the transition metal had little effect on these energies.

Compounds of the type $[AuX(PPh_3)_x]$, where X = Cl, NO_3, or ClO_4, also show little variation where $x = 1$, 2, or 3, in agreement with Battistoni *et al.*, but the f.w.h.m. value does increase, possibly due to the more ionic nature of the compounds with higher values of x. When $x = 4$, however, the Au $4f_{\frac{7}{2}}$ binding energy is not affected but the P $2p$ binding energy drops, possibly due to the ionic nature of this species (Table 2). Chlorine $2p$ energies appear to decrease more rapidly than phosphine levels as the number of phosphine groups increases.

Gold(III) complexes of the form $[AuX_3L]$ were found to be stable in the *X*-ray beam and gave consistently higher values of Au $4f_{\frac{7}{2}}$ binding energies (Table 3), indicating that the technique can be used, in a related series of complexes at least, to determine oxidation states. Halogen and phosphorus binding energies were also increased compared to the gold(I) complexes.

Gold Thiol Complexes.—Most but not all gold thiol complexes are complexes of gold(I), and the results obtained give a consistent value of *ca.* 84.7 eV for Au $4f_{\frac{7}{2}}$. Since there is some ambiguity in the assignment of the C_{1s} values, relative values in the series and comparisons with previous tables can only be very approximate. Gold cysteine, glutathione, and penicillamine all give somewhat larger values of f.w.h.m. than the other compounds and it seems likely that these are polymeric species.[1-3] Consequently, since there is no evidence of decomposition with time, it seems most likely that this breadth is caused by the polymer, either as a result of different sites or some strain effect. Gold(III) penicillamine has a higher Au $4f_{\frac{7}{2}}$ binding energy, in agreement with the results for other gold(III) species.

Binding Energies of Complexing Groups.—Complexation of phosphorus, sulphur, chloride, or bromide to gold gives rise to changes in their *X*-p.e. spectra which are too large to be due to random error (Table 5) and which are dependent on valency. Phosphorus, chloride, and bromide values change in the expected way, suggesting that electron density is progressively removed from the ligand as the metal-ion charge increases. The effect is largest for the negatively charged halides. The free-ligand value for sulphur is a combination of the result for cysteine (–SH) and cystine (–S–S) and, consequently, does not refer to free S^- as does the halide result. Nevertheless, the sulphur binding energy actually falls from Au^I to Au^{III}, suggesting that the gold(III)–sulphur complex is more ionic than the gold(I) complexes. The unidentate halide and phosphine ligands are probably approximately sp^3 hybridised in gold(III) complexes. The sulphur compounds contain more complex ligands, which may force a less favourable combination of sulphur orbitals to be employed to compensate for geometric requirements. However, until sufficient gold(III) thiols can be synthesised and characterised, this latter point must remain tentative.

TABLE 5

Comparison of the binding energies (eV) of atoms complexed to gold in gold(I) and gold(III) complexes and their uncomplexed form. For an explanation of the nature of the uncomplexed form see text

	Unbound	Au^I	Au^{III}
P 2*p*	131.1	131.9	132.4
S 2*p*	163.4	163.5	163.1
Cl 2*p*	197.5	198.7	199.2 $RAuCl_3$ 199.1 $R'^+AuCl_4^-$
Br 3*p*		182.1	182.6 $RAuBr_3$ 182.5 $R'^+AuBr_4^-$

$R = PEt_3$, $R' = NEt_4$.

Thus, using the Au $4f_{\frac{7}{2}}$ binding energy, the oxidation state of the gold can be readily identified. However, in the case of the gold(I) phosphines, the method used did not identify the different co-ordination numbers of gold(I) in the complexes as does Mössbauer spectroscopy.[5]

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