# Studies of Mixed-valence States in Three-dimensional Halogen-bridged Gold Compounds, $Cs_2Au^IAu^{III}X_6$ (X = Cl, Br or I). Part 2.[1] X-Ray Photoelectron Spectroscopic Study‡

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The mixed-valence states in $Cs_2Au^IAu^{III}X_6$ (X = Cl, Br or I) were systematically studied by X-ray photoelectron spectroscopy of the Au 4f region for the first time. The gold valence states in halogeno complexes of $Au^I$ and $Au^{III}$ were also studied. In $Cs_2Au_2X_6$ the difference between the oxidation state of $Au^I$ and that of $Au^{III}$ decreases as the covalency of the $-Au^I-X-Au^{III}-X-$ bonds increases in the order X = Cl < Br < I, because the charge-transfer interaction between $Au^I$ and $Au^{III}$ through the bridging halogen becomes stronger in this order. In the non-stoichiometric $CsAu_{0.6}Br_{2.6}$ the oxidation state of Au is considered to be almost homogeneous.

The technique of X-ray photoelectron spectroscopy (XPS) has been suggested to be an appropriate tool for probing the electronic structure of mixed-valence compounds.[2] Halogen-bridged one-dimensional $M^{II}-M^{IV}$ mixed-valence complexes of Pt, Pd and Ni have been investigated intensively from the viewpoints of physics and chemistry as a model of one-dimensional electronic systems,[3,4] and XPS has been employed.[5–7] On the other hand, to our knowledge, little XPS work on the $Au^I-Au^{III}$ mixed-valence complexes has been done.[8,9] In the preceding paper[1] we have mentioned an important feature that there are anisotropic three-dimensional $-X-Au^I-X-Au^{III}-$ networks in the structure of the Cs–Au–X mixed-valence system and also reported on a new non-stoichiometric caesium bromoaurate, $CsAu_{0.6}Br_{2.6}$ (cubic phase of Cs–Au–Br system). The purposes of the present study were systematically to investigate the mixed-valence states in $Cs_2Au_2X_6$ by changing the bridging halogen X from Cl to Br to I as a method for modifying the anisotropic charge-transfer interaction between $Au^I$ and $Au^{III}$ through the bridge, to investigate the gold valence state in the cubic phase of the Cs–Au–Br system, and to investigate the oxidation states in halogeno complexes of $Au^I$ and $Au^{III}$ by means of XPS measurements.

## Experimental

*Preparation of Gold Compounds.*—(*a*) $Cs_2Au_2Cl_6$. The mixed-valence compound $Cs_2Au_2Cl_6$ was prepared by the method described in ref. 10 (Found: Au, 44.9; Cs, 30.7. Calc. for $Au_2Cl_6Cs_2$: Au, 45.2; Cs, 30.5%).

(*b*) $Cs_2Au_2Br_6$. The mixed-valence compound $Cs_2Au_2Br_6$ was prepared by the method described in the preceding paper.[1]

(*c*) $CsAu_{0.6}Br_{2.6}$. The non-stoichiometric caesium bromoaurate was prepared by the method described in the preceding paper.[1]

(*d*) $Cs_2Au_2I_6$. An aqueous solution of CsI (0.015 mol) was slowly added to an aqueous solution of $HAuCl_4 \cdot 4H_2O$ (0.0025 mmol) at ice-bath temperature. The black compound $Cs_2Au_2I_6$ was formed, filtered off, washed with a dilute hydroiodic acid, and then dried in a vacuum desiccator for several days (100% yield) (Found: Au, 27.6; Cs, 18.7. Calc. for $Au_2Cs_2I_6$: Au, 27.7; Cs, 18.7%).

(*e*) $Cs[AuCl_4]$. A saturated aqueous solution of CsCl was added to a dilute HCl solution (3%) of $HAuCl_4 \cdot 4H_2O$ at ice-bath temperature. The yellow complex $Cs[AuCl_4] \cdot nH_2O$ was immediately formed. It was filtered off, washed with cold water, and then dried in a vacuum desiccator for several days. In this manner, the anhydrous complex $Cs[AuCl_4]$ was obtained (90% yield).

(*f*) $Cs[AuBr_4]$. An aqueous solution of CsBr (0.012 mol) was slowly added to a dilute HCl solution (3%) of $HaAuCl_4 \cdot 4H_2O$ (0.003 mol) at ice-bath temperatures. The red-brown complex $Cs[AuBr_4]$ was formed, filtered off, washed with cold water, and then dried in a vacuum desiccator for several days (95% yield).

(*g*) $[NBu^n_4][AuX_4]$ (X = Cl, Br *or* I). These salts were prepared by the methods described in the literature[11,12] (Found: C, 32.90; H, 6.25; Cl, 24.3; N, 2.40. Calc. for $C_{16}H_{36}AuCl_4N$: C, 33.05; H, 6.25; Cl, 24.4; N, 2.40. Found: C, 25.55; H, 4.75; Br, 42.4; N, 1.75. Calc. for $C_{16}H_{36}AuBr_4N$: C, 25.30; H, 4.80; Br, 42.1; N, 1.85. Found: C, 20.30; H, 3.75; I, 53.3; N, 1.50. Calc. for $C_{16}H_{36}AuI_4N$: C, 20.30; H, 3.80; I, 53.6; N, 1.50%).

(*h*) $[NBu^n_4][AuX_2]$ (X = Cl, Br *or* I). The bromide and iodide were prepared by the methods of Braunstein and Clark.[13] For the preparation of $[NBu^n_4][AuCl_2]$, their method was modified. We used phenylhydrazinium chloride in an anhydrous ethanol solution of hydrogen chloride instead of in absolute ethanol (Found: C, 37.45; H, 7.10; Cl, 13.7; N, 2.75. Calc. for $C_{16}H_{36}AuCl_2N$: C, 37.65; H, 7.10; Cl, 13.9; N, 2.75. Found: C, 31.95; H, 6.00; Br, 26.6; N, 2.30. Calc. for $C_{16}H_{36}AuBr_2N$: C, 32.05; H, 6.05; Br, 26.7; N, 2.35. Found: C, 27.65; H, 5.25; I, 36.9; N, 1.95. Calc. for $C_{16}H_{36}AuI_2N$: C, 27.70; H, 5.25; I, 36.6; N, 2.00%).

(*i*) AuCl *and* AuI. Gold(I) chloride and iodide were prepared by the methods described in the literature.[14]

*X-Ray analysis.*—Powder X-ray diffraction profiles were obtained at room temperature for all the compounds mentioned above. Each profile was in good agreement with that calculated from previous X-ray work.[14–16]

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‡ *Non-SI units employed:* eV ≈ 1.60 × $10^{-19}$ J; Torr ≈ 133 Pa.

**Table 1** Binding energies (eV) for the 4f region of gold

| | $4f_{\frac{5}{2}}$ | | $4f_{\frac{7}{2}}$ | |
|---|---|---|---|---|
| Compound | $Au^{III}$ | $Au^{I}$ | $Au^{III}$ | $Au^{I}$ |
| $Cs_2Au_2Cl_6$ [a,b] | 90.0 | 88.2 | 86.5 | 84.7 |
| $AuCl$ [a,b] | | 88.5 | | 84.8 |
| $[NBu^n_4][AuCl_2]$ [a,c] | | 88.3 | | 84.7 |
| $[NEt_4][AuCl_2]$ [d] | | — | | 84.8 |
| $[NBu^n_4][AuCl_4]$ [a,c] | 91.0 | | 87.4 | |
| $Cs[AuCl_4]$ [a,b] | 91.4 | | 87.7 | |
| $[NEt_4][AuCl_4]$ [d] | — | | 87.6 | |
| $Cs_2Au_2Br_5$ [a,b] | 89.4 | 88.2 | 85.8 | 84.6 |
| $CsAu_{0.6}Br_{2.6}$ [a,b] | 90.1 | | 86.5 | |
| $[NBu^n_4][AuBr_2]$ [a,c] | | 88.5 | | 84.9 |
| $[NEt_4][AuBr_2]$ [d] | | — | | 84.3 |
| $[NBu^n_4][AuBr_4]$ [a,c] | 90.8 | | 87.2 | |
| $Cs[AuBr_4]$ [a,b] | 90.6 | | 87.0 | |
| $[NEt_4][AuBr_4]$ [d] | — | | 86.7 | |
| $Cs_2Au_2I_6$ [a,b] | 88.4 | | 84.8 | |
| $Cs_2Au_2I_6$ [a,b] | 89.1 | 88.2 | 85.5 | 84.6 |
| $AuI$ [a,b] | | 88.3 | | 84.6 |
| $[NBu^n_4][AuI_2]$ [a,c] | | 88.6 | | 85.0 |
| $[NEt_4][AuI_2]$ [d] | | — | | 84.3 |
| $[NBu^n_4][AuI_4]$ [a,c] | 88.5 | | 84.9 | |
| $[NEt_4][AuI_4]$ [d] | — | | 84.3 | |

[a] Binding energies are accurate to ±0.15 eV. [b] Binding energies corrected by comparison with C 1s energy set at 285.0 eV for the hydrocarbon contamination. [c] Binding energies corrected by comparison with C 1s energy set at 285.3 eV for alkyl carbon in $[NBu^n_4]^+$. [d] From ref. 18. As more than one datum is given in ref. 18, the values quoted are averages. Binding energies are corrected by comparison with the C 1s energy set at 285.3 eV for alkyl carbon in $[NEt_4]^+$. Binding energies of $4f_{\frac{5}{2}}$ are not given in ref. 18.

*X-Ray Photoelectron Spectra.*—The X-ray photoelectron spectra were obtained on a DuPont ESCA 650B electron spectrometer (Shimazu Seisakusho), the source vacuum being $\approx 10^{-7}$ Torr, with a Mg-Kα X-ray source (1253.6 eV) at room temperature. Binding energies were measured relative to the C 1s peak (285.0 eV) due to hydrocarbon contamination which built up slowly on the surface under these operating conditions or to the C 1s peak (285.3 eV) for the alkyl carbon in tetrabutylammonium gold halides, in agreement with previous work.[17,18]

## Results and Discussion

The observed binding energies in the Au 4f region are given in Table 1. Fig. 1 shows the XPS spectra of this region for $Cs_2Au_2X_6$ (X = Cl, Br or I). As can be seen, the observed spectra for $Cs_2Au_2Cl_6$ and $Cs_2Au_2Br_6$ can be resolved into signals for $Au^{I}$ and $Au^{III}$, the latter ionizing at the higher energy. The intensity of the gold(III) signal is a little smaller than that of gold(I), probably due to the partial decomposition ($Au^{III}$ is partially reduced to $Au^{I}$) caused by the X-ray beam. For $Cs_2Au_2I_6$ the two gold sites were not satisfactorily resolved, though it is obvious from its powder[19] and our preliminary single-crystal[20] X-ray analyses that two sites are present. This doublet is very broad having a full width at half-maximum (f.w.h.m.) of approximately 2.6 eV. The doublets of $[NBu^n_4][AuI_2]$, AuI and $[NBu^n_4][AuI_4]$ are much narrower having widths of about 1.8 eV. The broad peak observed for $Cs_2Au_2I_6$ can be attributed to the contributions from both gold-(I) and -(III) sites giving rise to two overlapping signals separated by about 0.9 eV. According to our very recent work using a VG ESCA MKII electron spectrometer, the XPS spectrum for $Cs_2Au_2I_6$ could be resolved into signals for $Au^{I}$ and $Au^{III}$, as shown in Table 1. Thus, it is obvious that the two oxidation states exist in $Cs_2Au_2I_6$. Fig. 1 also shows that the difference in binding energy of the 4f signal between $Au^{I}$ and $Au^{III}$ decreases in the series $Cs_2Au_2Cl_6 \longrightarrow Cs_2Au_2Br_6 \longrightarrow Cs_2Au_2I_6$. This may be explained as follows. As the covalency of the $-Au^{I}-X-Au^{III}-X-$ bonds increases in the order X = Cl < Br < I, the charge-transfer interaction between the electronic state of $Au^{I}$ and that of $Au^{III}$ through the bridging halogen becomes stronger.

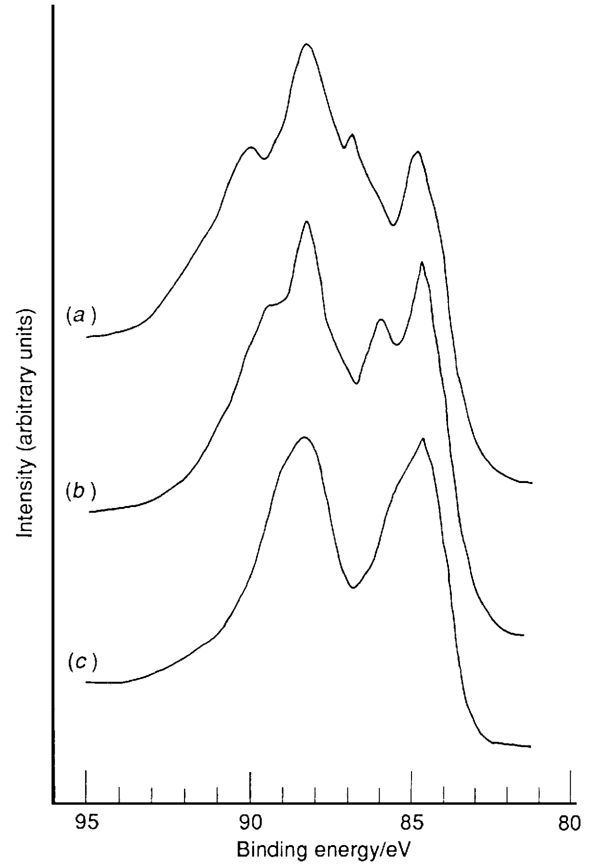

**Fig. 1** The XPS spectra in the Au 4f region of the mixed-valence compounds (*a*) $Cs_2Au_2Cl_6$, (*b*) $Cs_2Au_2Br_6$ and (*c*) $Cs_2Au_2I_6$

The binding energies $4f_{\frac{5}{2}}$ and $4f_{\frac{7}{2}}$ of $Au^{III}$ in $Cs_2Au_2X_6$ decrease in the order X = Cl > Br > I, while those of $Au^{I}$ are constant in going from X = Cl to I. This shows that the valence 5d-orbital population of $Au^{I}$ remains unchanged from X = Cl to I.

In the preceding paper[1] we referred to the crystal structures of $Cs_2Au_2X_6$ (X = Cl, Br or I), in which there are anisotropic three-dimensional $-X-Au^{I}-X-Au^{III}-$ networks. Therefore, also in the charge-transfer interaction between $Au^{I}$ and $Au^{III}$ through the bridging halogen X, it can be considered that there should be some anisotropy. We suppose that the charge-transfer interaction should be stronger in the *xy* plane ($\perp c$ axis) than in the *z* direction ($\parallel c$ axis) because the $5d_{x^2-y^2}$ orbital of the $[Au^{III}Cl_4]^-$ ion is unfilled in contrast to the $5d_{z^2}$ orbital which is filled. The charge-transfer interaction is considered to arise mainly from an overlap between the $5d_{x^2-y^2}$ orbitals of $Au^{I}$ and $Au^{III}$ through p orbitals of the bridging halogens. On this basis the lack of a shift in binding energy of the gold(I) signal of $Cs_2Au_2X_6$ from X = Cl to I can be explained as follows.

The decrease and the increase in the valence $5d_{x^2-y^2}$-orbital population of $Au^{I}$ occur simultaneously in going from $Cs_2Au_2Cl_6$ to $Cs_2Au_2I_6$. The former and the latter are due to the increase in the strength of the charge-transfer interaction and to the increase in the strength of the ligand-to-metal electron σ donation in the *xy* plane, respectively. The experimental result that the binding energies $4f_{\frac{5}{2}}$ and $4f_{\frac{7}{2}}$ of $Au^{I}$ are constant in going from $Cs_2Au_2Cl_6$ to $Cs_2Au_2I_6$ can be explained by assuming that the increase and the decrease in the valence-orbital population of $Au^{I}$ in going from $Cs_2Au_2Cl_6$ to $Cs_2Au_2I_6$ are compensated.

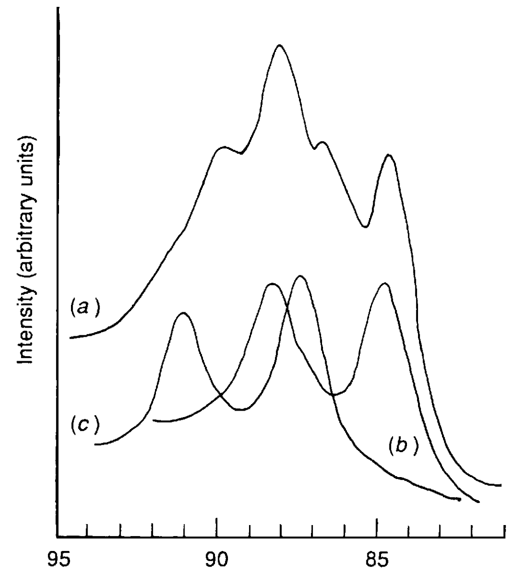

**Fig. 2** The XPS spectra in the Au 4f region of (*a*) $Cs_2Au_2Cl_6$, (*b*) $[NBu^n_4][AuCl_2]$ and (*c*) $[NBu^n_4][AuCl_4]$

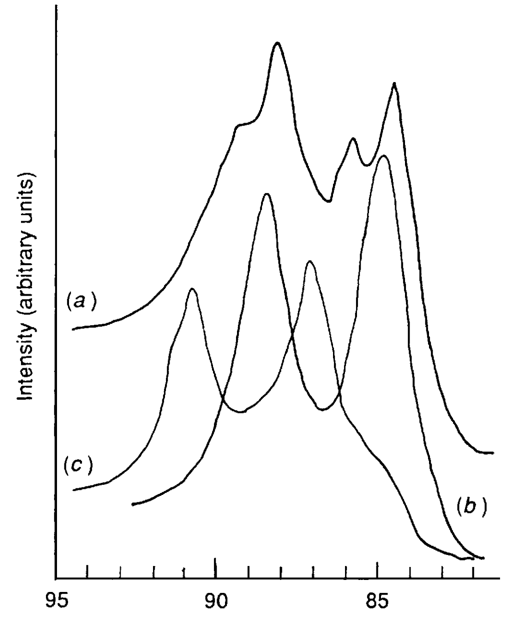

**Fig. 3** The XPS spectra in the Au 4f region of (*a*) $Cs_2Au_2Br_6$, (*b*) $[NBu^n_4][AuBr_2]$ and (*c*) $[NBu^n_4][AuBr_4]$

Fig. 2 shows the XPS spectra of the Au 4f region for $Cs_2Au_2Cl_6$ and the control complexes, $[NBu^n_4][AuCl_2]$ and $[NBu^n_4][AuCl_4]$. The binding energies $4f_{7/2}$ and $4f_{5/2}$ of $Au^I$ in $Cs_2Au_2Cl_6$ are almost equal to those of the chlorogold(I) complex. On the other hand, there is a significant difference between the binding energy of $Au^{III}$ in $Cs_2Au_2Cl_6$ and that of the chlorogold(III) complex, the former being 1.0 eV smaller. These behaviours of $Au^I$ and $Au^{III}$ are interpreted as follows. When the linear $[Au^ICl_2]^-$ and the square-planar $[Au^{III}Cl_4]^-$ are stacked alternately and three-dimensional $-X-Au^I-X-Au^{III}-$ networks are formed, the charge transfer from $Au^I$ to $Au^{III}$ through the bridging halogen Cl and the ligand-to-metal electron $\sigma$ donation from the ligand Cl in $[Au^{III}Cl_4]^-$ to $Au^I$ occurs in the *xy* plane. The lack of a difference in binding energy of $Au^I$ between $Cs_2Au_2Cl_6$ and the chlorogold(I) complex suggests that the quantity of the charge transfer from $Au^I$ to $Au^{III}$ in the *xy* plane is equal to that of that (ligand-to-metal electron $\sigma$ donation) in the *xy* plane from the ligand Cl in $[Au^{III}Cl_4]^-$ to $Au^I$. On the other hand, the difference in binding energy of $Au^{III}$ between $Cs_2Au_2Cl_6$ and the chlorogold(III) complex suggests that the amount of electronic charge flow into $Au^{III}$ is larger than that from $Au^{III}$. The charge flow into $Au^{III}$ is mainly caused by the charge transfer from $Au^I$ through the bridging halogen Cl in the *xy* plane and by the ligand-to-metal electron $\sigma$ donation in the *z* direction from the ligand Cl in $[Au^ICl_2]^-$ to $Au^{III}$. The charge outflow from $Au^{III}$ is caused only by the increase in $Au^{III}$–Cl distance in $[Au^{III}Cl_4]^-$ in the *xy* plane.* However, we consider that the amount of charge outflow caused by the removal of the halogen from $Au^{III}$ is small. The difference in the binding energy of $Au^{III}$ between $Cs_2Au_2Cl_6$ and the chlorogold(III) complex supports this consideration.

However, Robin and Day[21] suggested that the intervalence charge-transfer transition from a filled $d_{z^2}$-orbital of $Au^I$ to the unfilled $d_{x^2-y^2}$ orbital of $Au^{III}$ should occur in the *xy* plane, but reported that the intervalence charge-transfer absorption band of $Cs_2Au_2Cl_6$ was observed with light polarized parallel to the *c* axis. Their result is a puzzle for us. In order to elucidate this problem, detailed measurements of the polarized reflectance spectra of $Cs_2Au_2X_6$ (X = Cl, Br or I) are indispensable and in progress.

Also in the case of $Cs_2Au_2Br_6$ (Fig. 3), a difference in the binding energy of $Au^{III}$ between $Cs_2Au_2Br_6$ and the bromogold(III) complex but no difference in the binding energy of $Au^I$ between $Cs_2Au_2Br_6$ and the bromogold(I) complex were observed. Explanations for this behaviour are similar to those for $Cs_2Au_2Cl_6$ described above. The observed difference in the binding energy of $Au^{III}$ is 1.4 eV. The charge-transfer interaction in $Cs_2Au_2X_6$ (X = Cl, Br or I) will be evaluated below using the XPS results.

As an indication of the strength of the charge-transfer interaction, we adopted the expression (1). $\delta(M)$ is the

$$\Gamma = \delta(M)/\delta(S) \qquad (1)$$

difference in binding energy of the Au 4f signal between $Au^I$ and $Au^{III}$ in $Cs_2Au_2X_6$ and $\delta(S)$ is the difference in binding energy of this signal between $[Au^IX_2]^-$ and $[Au^{III}X_4]^-$. If we imagine a hypothetical state with $\Gamma = 1$, there is no interation between $Au^I$ and $Au^{III}$ (Robin–Day class I mixed-valence system[21]). If $\Gamma = 0$, the oxidation states of $Au^I$ and $Au^{III}$ are indistinguishable and that of Au is +II (Robin–Day class III mixed-valence system[21]). From the values in Table 1 we obtain $\Gamma$ (X = Cl) = 0.64 and $\Gamma$ (X = Br) = 0.55, where the binding energies of the Au 4f signal used for calculating $\delta(S)$ are the average values for the listed complexes. This indicates that the charge-transfer interaction in $Cs_2Au_2Br_6$ is stronger than that in $Cs_2Au_2Cl_6$. In the case of $Cs_2Au_2I_6$ (Fig. 4), the value of $\Gamma$ cannot be estimated because there is no difference in binding energy of the Au 4f signal between $[NBu^n_4][AuI_2]$ and $[NBu^n_4][AuI_4]$.

Fig. 5 shows the XPS spectra of halogenogold(III) complexes. It is immediately obvious that the binding energy of the Au 4f signal in $[Au^{III}X_4]^-$ is shifted to lower energy in the order $X = Cl \longrightarrow Br \longrightarrow I$. This behaviour can be explained as follows. A decrease in the binding energy of the Au 4f electrons is caused by an increase in Au 5d population. Considering $5d6s6p^2$ hybridization, an increase in the covalency of the $Au^{III}$–X bond in the order $X = Cl \longrightarrow Br \longrightarrow I$ causes an increase in $5d_{x^2-y^2}$ population. As can be seen from Fig. 4, the binding energy of the Au 4f signal of $[NBu^n_4][AuI_4]$ is almost equal to that of

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* When $[Au^ICl_2]^-$ and $[Au^{III}Cl_4]^-$ are stacked alternately the ligand Cl in $[Au^{III}Cl_4]^-$ co-ordinates to $Au^I$ and then the electronic charge in $Au^I$ is transferred to $Au^{III}$ by charge-transfer interaction. Here the valence of Au in $[Au^{III}Cl_4]^-$ would change from +3 to $+(3 - \beta)$ $(0 < \beta < 1)$. Hence the $Au^{III}$–Cl distance for $[Au^{III}Cl_4]^-$ in the mixed-valence compound $Cs_2Au_2Cl_6$ would be longer than that in gold(III) complex $[AuCl_4]^-$.

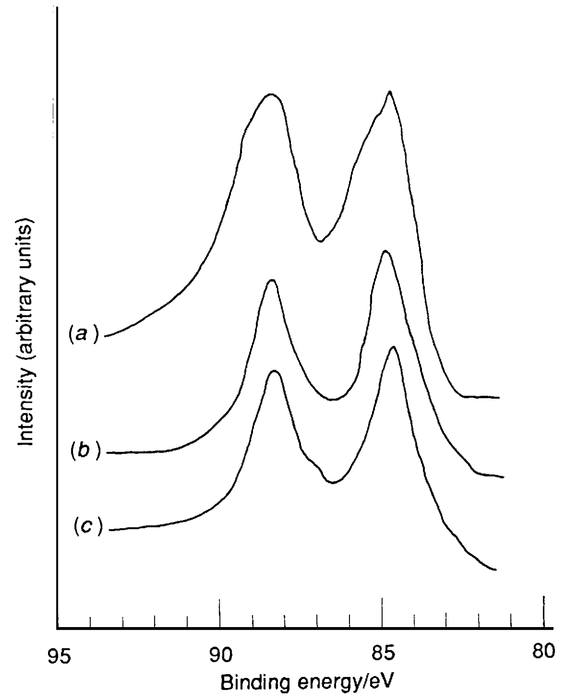

**Fig. 4** The XPS spectra in the Au 4f region of (*a*) $Cs_2Au_2I_6$, (*b*) $[NBu^n{}_4][AuI_2]$ and (*c*) $[NBu^n{}_4][AuI_4]$

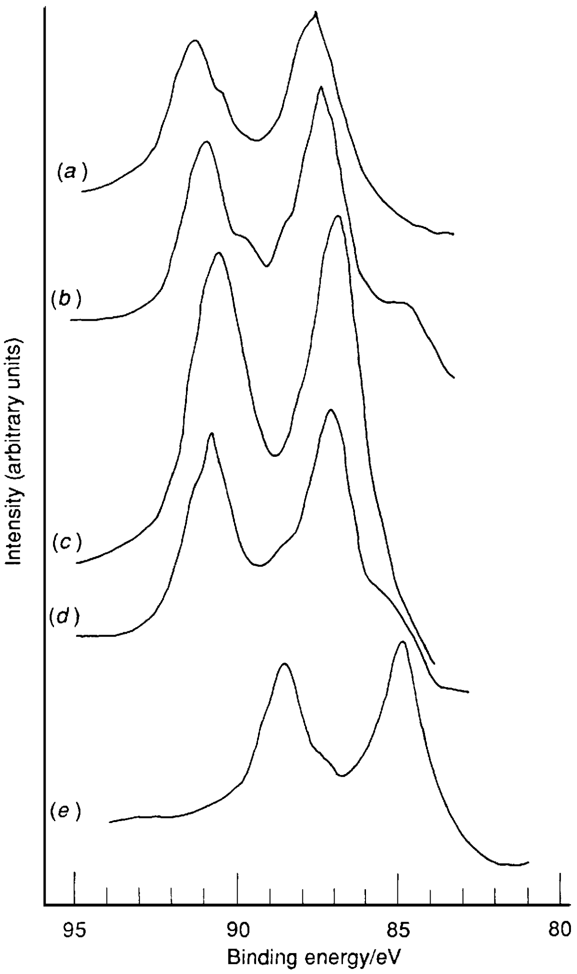

**Fig. 5** The XPS spectra in the Au 4f region of the halogenogold(III) complexes (*a*) $Cs[AuCl_4]$, (*b*) $[NBu^n{}_4][AuCl_4]$, (*c*) $Cs[AuBr_4]$, (*d*) $[NBu^n{}_4][AuBr_4]$ and (*e*) $[NBu^n{}_4][AuI_4]$

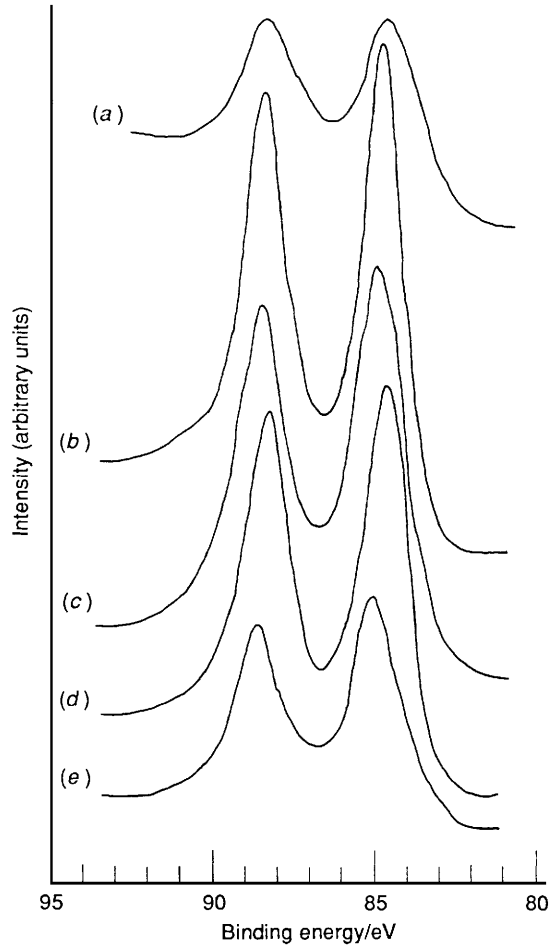

**Fig. 6** The XPS spectra in the Au 4f region of the halogenogold(I) complexes (*a*) $[NBu^n{}_4][AuCl_2]$, (*b*) AuCl, (*c*) $[NBu^n{}_4][AuBr_2]$, (*d*) AuI and (*e*) $[NBu^n{}_4][AuI_2]$

$[NBu^n{}_4][AuI_2]$. From this, the amount of the charge transfer from $I^-$ to $5d_{x^2-y^2}$ of $Au^{III}$ is expected to be considerably large. Therefore, the oxidation state of Au in $[NBu^n{}_4][AuI_4]$ is close to $Au^I$. The atomic Au $5d_{x^2-y^2}$ population of the molecular orbitals in $[NBu^n{}_4][AuI_4]$ is considered to be close to 2.0.

On the other hand, the binding energies of halogenogold(I) complexes are constant despite changing halide ion $X^-$ in $[AuX_2]^-$ and AuX (Fig. 6). Gold(I) complexes have linear two co-ordinate stereochemistry much more commonly than complexes of $Cu^I$ or $Ag^I$. Whether $6s6p_z$ or $5d_{z^2}$ hybridization in such a linear co-ordination is favourable for $Au^I$ has been discussed in many papers.[22–26] The electronic charge on the halide would be transferred mainly to the 6s or $6p_z$ orbital of $Au^I$. The amount of this charge transfer (ligand-to-metal electron $\sigma$ donation) is expected to increase in the order $Cl < Br < I$ for X in $[AuX_2]^-$. However, the 6s- or 6p-orbital contribution to the shielding of the 4f electrons from the nucleus is smaller than the 5d-orbital one. It is, therefore, difficult to estimate the 6s or $6p_z$ population by XPS measurements of the Au 4f region. We suppose that $^{197}Au$ Mössbauer spectroscopy might be a more useful tool for probing the electronic structure of 6s or $6p_z$ level.

Fig. 7 shows the spectrum of the cubic phase of the Cs–Au–Br system $CsAu_{0.6}Br_{2.6}$. In contrast to the tetragonal phase, $Cs_2Au_2Br_6$, only one doublet structure was observed. The discernible shoulders to lower energy of each of the $4f_{\frac{7}{2}}$ and $4f_{\frac{5}{2}}$ signals are due to partial decomposition to $Au^I$ caused by the X-ray beam since the $4f_{\frac{7}{2}}$ and $4f_{\frac{5}{2}}$ binding energies of the shoulder are almost equal to those of the gold(I) signal for $[NBu^n{}_4][AuBr_2]$. This phenomenon was also observed for

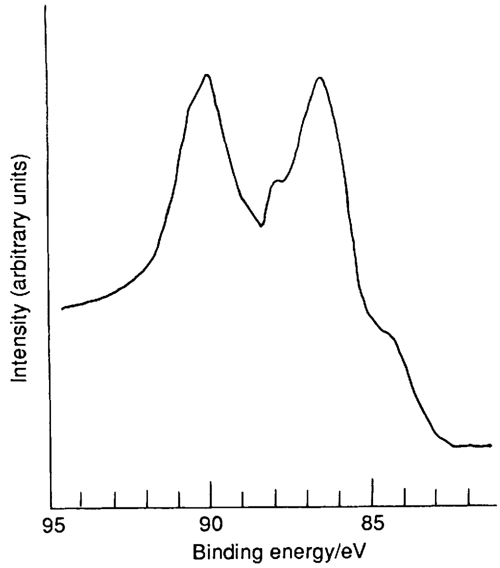

**Fig. 7** The XPS spectrum in the Au 4f region of the cubic phase $CsAu_{0.6}Br_{2.6}$

$[NBu^n_4][AuX_4]$ (X = Cl, Br or I). From only one doublet structure of this spectrum having a f.w.h.m. approximately equal to that of the spectrum of the gold-(I) or - (III) complex, the oxidation state of Au in the cubic phase is expected to be almost homogeneous. However, from its compositional ratio and Au 4f binding energies, the oxidation state of Au is supposed to be closer to $Au^{III}$ rather than the expected $Au^{II}$ and is a puzzle requiring further research.

## Conclusion

X-Ray photoelectron spectra were recorded to investigate the mixed-valence states of $Cs_2Au_2X_6$ (X = Cl, Br or I) for the first time. The difference between the oxidation states of $Au^I$ and $Au^{III}$ decreases in the order X = Cl > Br > I because the charge-transfer interaction in the *xy* plane becomes stronger in this order. In the cubic phase $CsAu_{0.6}Br_{2.6}$ the oxidation state of Au is considered to be almost homogeneous.

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