Studies of Mixed-valence States in Three-dimensional Halogen-bridged Gold Compounds, $Cs_2Au^IAu^{III}X_6$ (X = Cl, Br or I). Part 3.[1] Gold-197 Mössbauer Spectroscopic Study‡

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The mixed-valence states in $Cs_2Au^IAu^{III}X_6$ (X = Cl, Br or I) were studied by Mössbauer spectroscopy with the 77.34 keV γ-ray resonance of ^{197}Au. The states Au^I and Au^{III} could clearly be distinguished for all compounds. From an analysis of the isomer shifts and the quadrupole splittings the following conclusions were drawn: (1) the signs of the electric field gradient at Au^I and Au^{III} are negative and positive, respectively; (2) the charge-transfer interaction between Au^I and Au^{III} through the bridging halogen increases in the order X = Cl < Br < I and should be stronger in the *xy* plane (⊥ *c* axis) than in the *z* direction (∥ *c* axis); (3) for the cubic phase $CsAu_{0.6}Br_{2.6}$ only a single resonance line having a rather broad half-width was observed.

The family of compounds $Cs_2Au^IAu^{III}X_6$ (X = Cl, Br or I) is well known as a three-dimensional halogen-bridged class II mixed-valence system[2–6] according to the classification of Robin and Day.[5] In the present paper we report Mössbauer data for this system, which, taken together with previously published work[7–10] and the XPS data discussed in the preceding paper,[1] afford a useful insight into the electronic structure of these mixed-valence compounds. The 77.34 keV ^{197}Au Mössbauer resonance is very sensitive to the valence state and the chemical environment, and the gold compounds show a wide variation in quadrupole splitting and isomer shift.[11–14]

In the present paper we employ a method of changing the charge-transfer interaction in $Cs_2Au^IAu^{III}X_6$ which is the replacement of bridging halogen X = Cl → Br → I. The consequent changes in the isomer shifts and the quadrupole splittings of the gold-(I) and -(III) nuclei will provide some new information about the signs of the electric field gradient at these nuclei, the hybridization scheme, and the charge-transfer interactions between Au^I and Au^{III}. In the previous paper (XPS study)[1] we showed that the charge-transfer interaction should be stronger in the *xy* plane (⊥ *c* axis) than in the *z* direction (∥ *c* axis). The main purpose of this paper is to discuss the changes in the isomer shifts and quadrupole splittings of $Cs_2Au_2X_6$ (X = Cl, Br or I) on this basis.

Experimental

All the compounds were prepared by the methods described in Parts 1[15] and 2.[1]

Mössbauer spectroscopic measurements of the 77.34 keV transition in ^{197}Au were carried out with both source and absorber cooled to 16 K using a constant-acceleration spectrometer with a NaI(Tl) scintillation counter. The data were stored in a microcomputerized 512 multichannel analyser. A ^{197}Pt source was obtained by neutron irradiation of 98%-enriched platinum due to the nuclear reaction $^{196}Pt[n,r]^{197}Pt$ in the Kyoto University Reactor (KUR). The velocity scale was calibrated by taking spectra of body-centred cubic iron against a ^{57}Co source, both at room temperature. The observed spectra were analysed by use of a computer program including folding and least-squares fitting with Lorentzian lines.

Table 1 Gold-197 Mössbauer data for the mixed-valence compounds $Cs_2Au_2X_6$ (X = Cl, Br or I) and the cubic phase of the Cs–Au–Br system $CsAu_{0.6}Br_{2.6}$

Complex	i.s./mm s^{-1}	q.s./ mm s^{-1}	Γ/mm s^{-1}	*A* (%)	A^I/A^{III}
$Cs_2Au_2Cl_6$ (160 mg Au cm^{-2})*					
Au^I	0.03 ±0.05	5.06 ±0.05	2.04 ±0.08	44.9	
Au^{III}	1.38 ±0.05	0.76 ±0.05	2.14 ±0.08	55.1	0.82
$Cs_2Au_2Br_6$ (160 mg Au cm^{-2})*					
Au^I	0.21 ±0.05	4.57 ±0.05	1.81 ±0.08	32.3	
Au^{III}	1.12 ±0.05	1.37 ±0.05	2.43 ±0.08	67.7	0.49
$Cs_2Au_2I_6$ (160 mg Au cm^{-2})*					
Au^I	1.02 ±0.05	4.58 ±0.05	2.04 ±0.08	46.9	
Au^{III}	1.54 ±0.05	1.68 ±0.05	1.89 ±0.08	53.1	0.88
$CsAu_{0.6}Br_{2.6}$ (100 mg Au cm^{-2})*					
	1.51 ±0.05	—	2.73 ±0.08	—	—

* The absorber thickness of Au.

Results and Discussion

The observed ^{197}Au Mössbauer data, isomer shift (i.s.), quadrupole splitting (q.s.), half-width (Γ), and the intensity ratio (A^I/A^{III}) for the mixed-valence compounds $Cs_2Au_2X_6$ (X = Cl, Br or I), are given in Table 1. All i.s. values here are referenced to metallic gold foil. In order to refer these isomer shifts to gold in platinum, 1.20 mm s^{-1} have to be subtracted from the tabulated values. The ^{197}Au Mössbauer data for previously measured related gold compounds are given in Table 2. The observed ^{197}Au Mössbauer spectra are shown in Fig. 1. A best fit is obtained with two doublets, the outer with lower intensity being assigned to Au^I, the inner to Au^{III}. These assignments are similar to those previously reported[7–9] for $Cs_2Au_2Cl_6$ and not similar

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‡ *Non-SI units employed:* eV ≈ 1.60 × 10^{-19} J, a.u. ≈ 0.529 × 10^{-10} m.

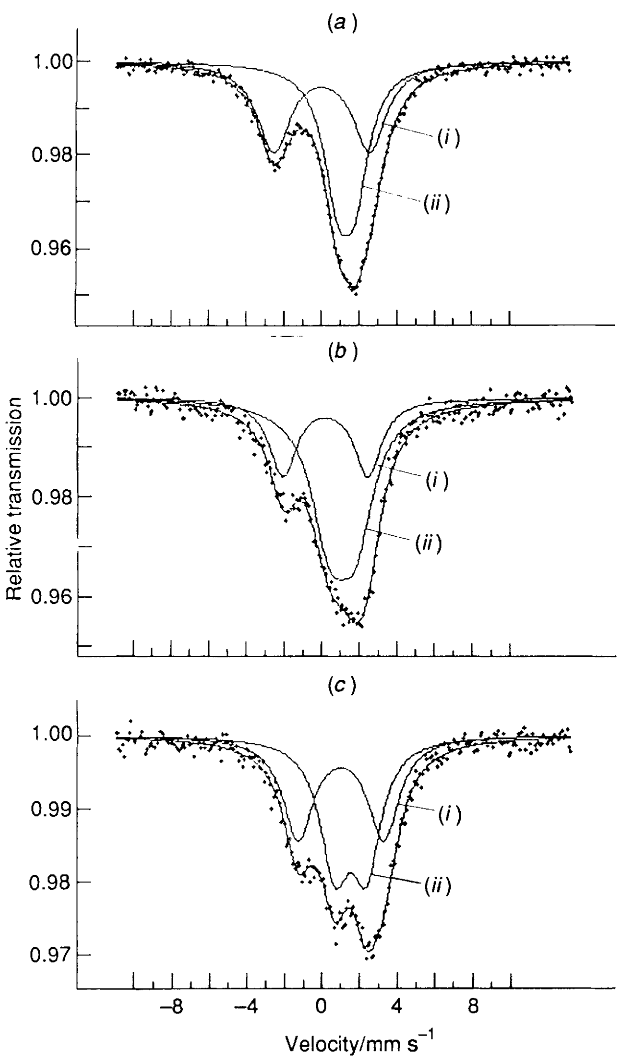

Fig. 1 Gold-197 Mössbauer spectra of the mixed-valence compounds (*a*) $Cs_2Au_2Cl_6$, (*b*) $Cs_2Au_2Br_6$ and (*c*) $Cs_2Au_2I_6$; (*i*) Au^I, (*ii*) Au^{III}

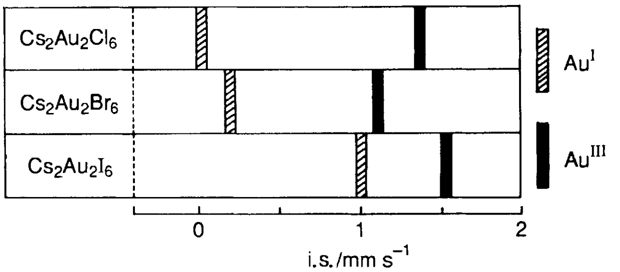

Fig. 2 Changes in the isomer shifts i.s.^{I} and i.s.^{III} for the gold-(I) and -(III) sites in $Cs_2Au_2X_6$ in going from X = Cl to I

to those[10] for $Cs_2Au_2Br_6$. In ref. 10, the doublet at low velocity was assigned to Au^I and that at high velocity to Au^{III}. The intensity ratio of the two components A^I/A^{III} should be 1.0:1 because of the Au^I/Au^{III} compositional ratio in stoichiometric $Cs_2Au_2X_6$. However, the experimental ratios are smaller than the expected ones. As is well known,[7,16,17] the unequal intensities are due to the difference in recoil-free fractions f^I and f^{III} for the gold-(I) and -(III) sites in $Cs_2Au_2X_6$. Since the Au^I is in two-fold (linear) ligand co-ordination and the Au^{III} in four-fold (square-planar) co-ordination,[3,6,18] the environment of the Au^{III} in $Cs_2Au_2X_6$ is more rigid than that of the Au^I. The mean-square vibrational amplitude of Au^{III} is considered, therefore, to be smaller than that of Au^I. The intensity ratio (A^I/A^{III}) for $Cs_2Au_2Cl_6$ will be discussed below using the isotropic thermal parameters B obtained from the X-ray measurement.[18]

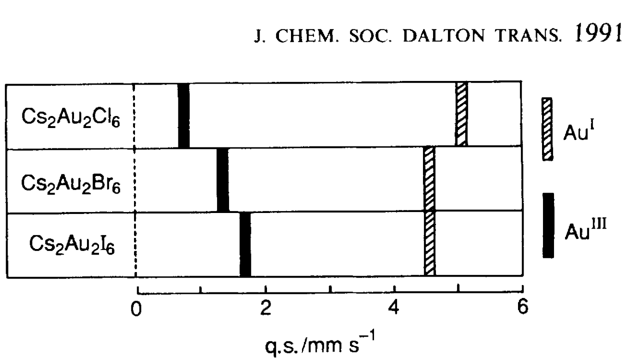

Fig. 3 Changes in the quadrupole splittings q.s.^{I} and q.s.^{III} for the gold-(I) and -(III) sites in $Cs_2Au_2X_6$ in going from X = Cl to I

From the value of the mean-square vibrational displacement u^2 [equation (1)], we obtain $u^2(Au^I) = 0.0223$ Å^2 and

$$u^2 = B/8\pi^2 \qquad (1)$$

$u^2(Au^{III}) = 0.0201$ Å^2 at 293 K, and for the ratio of the f factors, $f^I/f^{III} = \exp\{-K^2[u^2(Au^I) - u^2(Au^{III})]\} = 3.7 \times 10^{-2}:1$ where $K^2 = 1.5 \times 10^3$ Å^{-2} for the 77.34 keV γ-rays of ^{197}Au. In the limit of high temperatures we obtain approximately $f = \exp(-6E_R T/k_B\theta_D^2)$ where $T > \theta_D$. Debye temperatures θ_D of 99 and 104 K are obtained for Au^I and Au^{III}, respectively. For this, $E_R = 16.3 \times 10^{-3}$ eV was adopted. Debye temperatures obtained by this simple model are applicable to the low-temperature approximation ($T \ll \theta_D$), $f = \exp\{(-3E_R/2k_B\theta_D)\text{-}[1 + (2\pi^2/3)(T/\theta_D)^2]\}$ ($f^I = 0.034$, $f^{III} = 0.042$), and the value $f^I/f^{III} = 0.81$ may be compared with the experimental value $A^I/A^{III} = 0.82$ at 16 K (Table 1). The ratio of the f factors estimated from the X-ray diffraction measurements is in excellent agreement with the observed intensity ratio. In the cases of $Cs_2Au_2Br_6$ and $Cs_2Au_2I_6$ we cannot estimate the f values because there are no single-crystal X-ray data.

As can be seen from Fig. 1, the valence states of Au^I and Au^{III} are clearly distinguishable for all the compounds. In the case of $Cs_2Au_2I_6$ we could not distinguish satisfactorily between the valence states of Au^I and Au^{III} by XPS,[1,19] but the ^{197}Au Mössbauer spectrum can be well resolved into these components.

Information obtained from XPS of inner shells gives the chemical shift only ($4f_{5/2}$–$4f_{7/2}$ separation of a spin–orbit doublet is approximately constant ≈ 3.6 eV, regardless of the variation of the oxidation state of Au). On the other hand, Mössbauer spectroscopy provides two major parameters (*i.e.* i.s. and q.s.), which can be related to the populations and changes in population of the valence-shell orbitals. An i.s. is related to the total electron density on the nucleus (*i.e.* s-electron density), $\rho(0)$, and a q.s. reflects any anisotropy in the distribution of the electron density. Therefore, Mössbauer spectroscopy may be more suitable for detailed analysis of oxidation states than XPS of inner shells.

Fig. 2 shows the isomer shifts i.s.^{I} and i.s.^{III} for the gold-(I) and -(III) sites in $Cs_2Au_2X_6$ (X = Cl, Br or I). The difference in the i.s. values between Au^I and Au^{III} decreases in the order X = Cl > Br > I, which implies that the oxidation states of Au^I and Au^{III} in $Cs_2Au_2X_6$ tend to approach Au^{II} in this order. This behaviour suggests that the charge-transfer interaction between Au^I and Au^{III} becomes stronger in this order and is consistent with our XPS study.[1,19] This is mainly due to the increase in covalency of the $-Au^I-X-Au^{III}-X-$ bonds (the increase in overlap of filled $5d_{x^2-y^2}$ orbitals of Au^I and empty $5d_{x^2-y^2}$ orbitals of Au^{III} through p_x or p_y orbitals of the bridging halogen X) in the order X = Cl < Br < I. Also as shown in Fig. 2, i.s.^{I} increases in the order X = Cl < Br < I, while i.s.^{III} decreases from X = Cl to Br and increases from X = Br to I. As shown in Fig. 3, the quadrupole splitting q.s.^{III} increases in the order X = Cl < Br < I, on the other hand q.s.^{I} decreases slightly in this order. The changes in q.s.^{I} and q.s.^{III} in $Cs_2Au_2X_6$ are quite

Table 2 Gold-197 Mössbauer data (mm s^{-1})

Compound		i.s.	q.s.	Γ	Ref.
$Cs_2Au_2Cl_6$[a]	Au^{I}	0.13[b]	5.06	2.04	9
	Au^{III}	1.31[b]	1.00	1.88	
$Cs_2Au_2Cl_6$	Au^{I}	−1.07(3)[c]	5.04(6)		7
	Au^{III}	0.34(2)[c]	1.17(4)		
$Cs_2Au_2Br_6$	Au^{I}	−1.22[c]	3.84	1.88	10
	Au^{III}	0.54[c]	1.72	1.90	
$Cs_2AgAuCl_6$[d]		1.54[b]	0	2.33	9
$Cs_2AgAuCl_6$		0.32(1)[c]	0.86(2)		7
$Cs_2AgAuBr_6$		0.42[c]	0.99	2.18	10
$Cs_{1.5}(AuBr_4)(Br_3)_{0.2}Br_{0.3}$		0.53[c]	0.94	2.16	10
$[NBu^n_4][AuCl_2]$		0.31(7)[c]	5.93(7)		29
$[NBu^n_4][AuI_2]$		0.30(7)[c]	5.61(7)		29
$K[AuCl_4]$		0.81[c,e]	1.11[f]	1.76[e]	34
$K[AuBr_4]$		0.60[c,e]	1.13[f]	1.78[d]	34
$K[AuI_4]$		0.43[c,g]	1.28[h]	1.92[f]	34

[a] ±0.08 mm s^{-1}. [b] Relative to gold metal. [c] Relative to gold in platinum. [d] ±0.04 mm s^{-1}. [e] ±0.03 mm s^{-1}. [f] ±0.06 mm s^{-1}. [g] ±0.05 mm s^{-1}. [h] ±0.10 mm s^{-1}.

similar to the pressure-induced changes in $Cs_2Au_2Cl_6$ reported by Stanek and co-workers.[7,20] The charge-transfer interaction in $Cs_2Au_2Cl_6$ should become stronger with increasing pressure, which is consistent with the above similarity. However, their assumption that the signs of the electric field gradient (e.f.g.) at the gold-(I) and -(III) sites are positive and negative, respectively, is in disagreement with ours as described in the following paragraphs. As the charge-transfer interaction in $Cs_2Au_2X_6$ becomes stronger, q.s.^{III} increases while q.s.^{I} decreases. However, Katada *et al.*,[9] based on their experimental result that the q.s.^{III} of $Cs_2Ag^{I}Au^{III}Cl_6$ is smaller than that of $Cs_2Au^{I}Au^{III}Cl_6$, concluded that the interaction between two metal atoms in the 4d–5d mixed-metal compound $Cs_2Ag^{I}Au^{III}Cl_6$ is stronger than that in the 5d–5d mixed-valence compound $Cs_2Au^{I}Au^{III}Cl_6$. Their conclusion is, therefore, in conflict with our discussion and, moreover, Yamada and Tsuchida[21] did not reach such a conclusion. X-Ray absorption near-edge structure (XANES) spectra[22] suggest that the oxidation state of Au^{III} in $Cs_2Ag^{I}Au^{III}Cl_6$ is almost equal to that in $[NBu^n_4][Au^{III}Cl_4]$. Hence we are convinced that the charge-transfer interaction in the 4d–5d mixed-metal system is weaker than that in the 5d–5d mixed-valence system. In our previous paper (XPS study)[1] we showed that the charge-transfer interaction between Au^{I} and Au^{III} should be stronger in the *xy* plane than in the *z* direction. In the following paragraphs, the changes in q.s. and i.s. in $Cs_2Au_2X_6$ (X = Cl, Br or I) will be discussed on the basis of this view.

Q.s.^{I} *in* $Cs_2Au^{I}Au^{III}X_6$.—When the Mössbauer spectrum is a simple doublet the quadrupole splitting (q.s.) is given by equation (2), where *e* is the charge on the proton ($e > 0$), Q is the

$$\text{q.s.} = \tfrac{1}{2}eQV_{zz}\,(1 + \eta^2/3)^{\frac{1}{2}} \qquad (2)$$

nuclear quadrupole moment ($+0.59 \times 10^{-28}$ m^2 for the ground state of ^{197}Au), V_{zz} is the principal component of the e.f.g. (often designated as eq_{zz}), and η is the asymmetry parameter. For linear $[AuX_2]^-$ and square-planar $[AuX_4]^-$ ions we shall take η as zero. The concentration of negative charge in the *xy* plane makes the e.f.g. positive, and that on the *z* axis makes it negative. The sign of the e.f.g. at Au^{I} has been discussed in many papers.[7,23–31] The sign of the e.f.g. at Au^{I} in $KAu(CN)_2$ was determined by means of a single-crystal absorber.[32] However, in the case of the halogeno complexes $[AuX_2]^-$ (X = Cl, Br or I) the sign has not yet been determined by experiment. In the case of linear gold(I) ($5d^{10}$) complexes, it has been considered[23,24,26,29,31,32] that ^{197}Au Mössbauer data favour the sp hybridization scheme.* In this scheme the sign of the e.f.g. is expected to be negative. From the viewpoint of sp hybridization, with increasing σ-donor strength of the ligands in the order X = Cl < Br < I the atomic $6p_z$ population (negative contribution to the e.f.g.) of the molecular orbitals on the gold ion increases, and therefore the absolute value of the negative e.f.g. is expected to increase in this order. However, the experimental fact is the opposite. Mössbauer measurements on $[NBu^n_4][Au^{I}X_2]$ (X = Cl or I) reported by Braunstein *et al.*[31] have shown that q.s.^{I} (5.61 mm s^{-1}) when X = I is smaller than that (5.93 mm s^{-1}) when X = Cl. This anomalous order of q.s. values has also been noted for corresponding chloro- and iodo-complexes.[35] This discrepancy has been a puzzle for us. However, the SCF-MS-Xα study of $[Au^{I}X_2]^-$ (X = Cl, Br or I) reported by Bowmaker *et al.*[34] has showed that the $6p_z$ population increases from $[AuCl_2]^-$ to $[AuI_2]^-$, but there is a slight expansion in the $6p_z$ orbital from $[AuCl_2]^-$ to $[AuI_2]^-$ which results in a progressive decrease in the normalized e.f.g. for the $6p_z$ orbital (the main contribution to the e.f.g. comes from the electron density in the Au $6p_z$ orbital). This phenomenon is supposed to be closely related to the nephelauxetic series of ligands Cl < Br < I.

In the case of the mixed-valence compounds $Cs_2Au_2X_6$, q.s.^{I} decreases from X = Cl to Br and does not change from X = Br to I (Fig. 3). In the order X = Cl < Br < I for $Cs_2Au_2X_6$, both the charge-transfer interaction between the $5d_{x^2-y^2}$ orbitals of Au^{I} and Au^{III} and the σ donation of attached ligands in $[Au^{III}X_4]^-$ to $5d_{x^2-y^2}$ orbitals of Au^{I} are considered to become stronger. From the XPS study for $Cs_2Au_2X_6$,[1] it was found that the valence 5d-orbital population of Au^{I} does not change in going from X = Cl to I. Therefore, in the case of Au^{I}, the decrease in the valence 5d-orbital population, which is due to the increase in strength of the charge-transfer interaction (X = Cl < Br < I), and the increase in it due to the increase in the strength of the ligand-to-metal electron σ donation (X = Cl < Br < I), compensate each other in the *xy* plane. On the other hand, the charge-transfer interaction in the *z* direction should be weak. Therefore, the decrease in q.s.^{I} from X = Cl to Br is mainly due to the slight expansion in the $6p_z$ orbital which causes a significant reduction in the magnitude of the e.f.g. at the gold(I) site. Compared with q.s.^{I} in $[NBu^n_4][AuCl_2]$, the value in $Cs_2Au_2Cl_6$ is small. This may be explained as follows. The Au^{I}–Cl distance in $Cs_2Au_2Cl_6$ (2.281 Å) is longer than that in $[NBu^n_4][AuCl_2]$ (2.257 Å).† An increase in the Au^{I}–Cl distance causes a slight expansion in the $6p_z$ orbital and a decrease in the $6p_z$ orbital population. Thus, the electron density of the Au $6p_z$ orbital in $Cs_2Au_2Cl_6$, which is the main contribution to the e.f.g. at the gold(I) site, is smaller than that in $[NBu^n_4][AuCl_2]$. The similar behaviour of q.s.^{I} of $Cs_2Au_2I_6$ compared with that of $[NBu^n_4][AuI_2]$ can be explained in the same way. The lack of a shift in q.s.^{I} from $Cs_2Au_2Br_6$ to $Cs_2Au_2I_6$ can be interpreted as follows. From $Cs_2Au_2Br_6$ to $Cs_2Au_2I_6$ the $6p_z$ population of Au^{I} increases, while the $6p_z$ orbital of Au^{I} expands slightly. The effect of the expansion in the $6p_z$ orbital on the e.f.g. is supposed to be almost equal to the effect of the increase in the $6p_z$ population from $Cs_2Au_2Br_6$ to $Cs_2Au_2I_6$. This is consistent with the SCF-MS-Xα study[34] in which atomic orbital populations and orbital contributions to the e.f.g. for $[AuX_2]^-$ (X = Cl, Br or I) were estimated. The $6p_z$ orbital of Au plays a most important role in determining the magnitude and sign of the e.f.g. Though the atomic $6p_z$ orbital population becomes larger in the order X = Cl (0.328) < Br (0.338) < I (0.366), negative contributions of this orbital to the e.f.g. decrease from

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* However, we note that some workers[7,25,27,28,30,32–34] have considered that the partial presence of some d–s mixing cannot be excluded.

† The Au^{I}–X distances for $[AuX_2]^-$ in the Au^{I}–Au^{III} mixed-valence compounds $Cs_2[AuCl_2][AuCl_4]$, $Rb_2[AuBr_2][AuBr_4]$, and $K_2[AuI_2][AuI_4]$ are longer than those in $[NBu^n_4][AuCl_2]$, $[NBu^n_4][AuBr_2]$, and $[NBu^n_4][AuI_2]$, respectively.[36]

X = Cl (−8.2 a.u.) to Br (−7.8 a.u.) and remain unchanged from X = Br to I (−7.8 a.u.).

Q.s.$^{\mathrm{III}}$ *in* $\mathrm{Cs_2Au^{I}Au^{III}X_6}$.—Although a q.s.–i.s. correlation for Au$^{\mathrm{III}}$ is similar to that for Au$^{\mathrm{I}}$,[37] it is clear that the e.f.g. at Au$^{\mathrm{I}}$ must be different in sign from that at Au$^{\mathrm{III}}$. In square-planar gold(III) complexes the principal component of the e.f.g. must lie perpendicular to the *xy* plane ($5d_{x^2-y^2}$ hole, negative contribution to the e.f.g.). Increasing σ donation from ligands (into $5d_{x^2-y^2}$ and $6p_{x,y}$ orbitals) will induce an increasing positive contribution to the e.f.g. Since the experimental $\langle r^{-3}\rangle$ values have been found to be larger for 6p than for 5d electrons, the e.f.g. at Au$^{\mathrm{III}}$ is expected to be relatively small and presumably positive, and this has been confirmed for $\mathrm{K[Au(CN)_4]}$.[1] Mössbauer measurements in $\mathrm{K[AuX_4]}$ (X = Cl, Br or I) have shown that q.s.$^{\mathrm{III}}$ increases in the order X = Cl (1.11) < Br (1.13) < I (1.28 mm s^{-1}).[37] In this mixed-valence system the q.s.$^{\mathrm{III}}$ was found to increase in the order X = Cl (0.76) < Br (1.37) < I (1.68 mm s^{-1}). The q.s.$^{\mathrm{III}}$ of each of $\mathrm{Cs_2Au_2Br_6}$ and $\mathrm{Cs_2Au_2I_6}$ is larger than that of $\mathrm{K[AuBr_4]}$ and $\mathrm{K[AuI_4]}$, respectively, while q.s.$^{\mathrm{III}}$ of $\mathrm{Cs_2Au_2Cl_6}$ is smaller than that of $\mathrm{K[AuCl_4]}$. These trends can be explained as below. Because of a large increase in the unilateral electronic charge transfer from Au$^{\mathrm{I}}$ to Au$^{\mathrm{III}}$ in the *xy* plane (positive contribution to the e.f.g. at Au$^{\mathrm{III}}$) along the series of $\mathrm{Cs_2Au_2Cl_6}$ < $\mathrm{Cs_2Au_2Br_6}$ < $\mathrm{Cs_2Au_2I_6}$, the positive q.s.$^{\mathrm{III}}$ should increase along this series, in spite of an increase in the charge transfer from halogen p_z to the metal orbital (negative contribution to the e.f.g.). The fact that, in spite of this negative contribution, the q.s.$^{\mathrm{III}}$ of each of $\mathrm{Cs_2Au_2Br_6}$ and $\mathrm{Cs_2Au_2I_6}$ is larger than that of $\mathrm{K[AuBr_4]}$ and $\mathrm{K[AuI_4]}$, respectively, suggests that the charge-transfer interaction between Au$^{\mathrm{I}}$ and Au$^{\mathrm{III}}$ is stronger in the *xy* plane than in the *z* direction. In $\mathrm{Cs_2Au_2Cl_6}$ the opposite relation may be explained as follows. The charge-transfer interaction in $\mathrm{Cs_2Au_2Cl_6}$ is weaker than that in $\mathrm{Cs_2Au_2Br_6}$ or $\mathrm{Cs_2Au_2I_6}$. In the case of $\mathrm{Cs_2Au_2Cl_6}$, therefore, the effect of the expansion in $5d_{x^2-y^2}$ and $6p_{x,y}$ orbitals on the e.f.g. or the charge transfer from the halogen p_z orbital in $\mathrm{[AuX_2]^-}$ to the gold(III) orbital (each is a negative contribution to the e.f.g. at Au$^{\mathrm{III}}$) is negligible compared with transfer of electronic charge from Au$^{\mathrm{I}}$ to Au$^{\mathrm{III}}$ in the *xy* plane caused by the charge-transfer interaction (positive contribution to the e.f.g. at Au$^{\mathrm{III}}$).

As was noted in the previous section, the changes in q.s.$^{\mathrm{I}}$ and q.s.$^{\mathrm{III}}$ in $\mathrm{Cs_2Au_2X_6}$ in going from X = Cl to I are quite similar to the pressure-induced changes for X = Cl reported by Stanek.[7] From this similarity it can be considered that with increasing pressure the charge-transfer interaction for X = Cl becomes stronger in the *xy* plane. However, in the high-pressure Mössbauer study of $\mathrm{Cs_2Au_2Cl_6}$ the charge-transfer interaction was not taken into account for the pressure-induced changes, though the charge-transfer interaction plays a more important role in a mixed-valence system under high pressure than under ambient pressure. Moreover, despite the similarity of the changes in q.s.$^{\mathrm{I}}$ and q.s.$^{\mathrm{III}}$, Stanek's conclusion that the signs of the e.f.g. at Au$^{\mathrm{I}}$ and Au$^{\mathrm{III}}$ are positive and negative, respectively is in disagreement with ours. In his study the pressure-induced change in q.s.$^{\mathrm{I}}$ for $\mathrm{Cs_2Au_2Cl_6}$ was discussed on the basis of a ds-hybridization scheme for $\mathrm{[Au^{I}Cl_2]^-}$. The hybridization scheme in complexes of Au$^{\mathrm{I}}$ having the d^{10}-electron configuration has been the subject of considerable discussion (5d6s *vs.* 6s6p). Recently, however, most Mössbauer investigators favour the sp-hybridization scheme. Also, the pressure-induced change in q.s.$^{\mathrm{III}}$ for $\mathrm{Cs_2Au_2Cl_6}$ was discussed only on the basis of a decrease in σ-donor strength of the attached ligands in $\mathrm{[Au^{III}Cl_4]^-}$ due to the increase in the Au$^{\mathrm{III}}$–Cl distances within the *xy* plane. Since the charge-transfer interaction was not considered in the high-pressure study, Stanek's conclusion as to the signs of the e.f.g. at Au$^{\mathrm{I}}$ and Au$^{\mathrm{III}}$ is the opposite of ours.

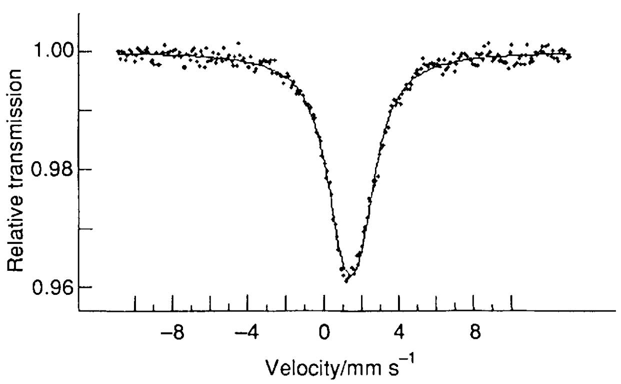

Fig. 4 Gold-197 Mössbauer spectrum of the cubic phase $\mathrm{CsAu_{0.6}Br_{2.6}}$

I.s.$^{\mathrm{I}}$ *and* i.s.$^{\mathrm{III}}$ *in* $\mathrm{Cs_2Au^{I}Au^{III}X_6}$.—The isomer shift (i.s.) is given by equation (3) where *C* is a constant containing nuclear parameters (>0), $\Delta\langle R^2\rangle$ is the change in the square of the nuclear radius between the excited and the ground states which has been estimated[38] as $+8.6 \times 10^{-3}$ fm^2 for ^{197}Au, and $\Delta\rho(0)$ is the difference between the contact densities of the source and the absorber.

$$\text{i.s.} = C\Delta\langle R^2\rangle\Delta\rho(0) \qquad (3)$$

For ^{197}Au, therefore, a positive shift in i.s. indicates an increase in the electron density at the nucleus, ρ(0). The valence-electron contribution to ρ(0) is well known to be affected in two ways: (*a*) increasing the s-electron population in the valence shell directly increases ρ(0); (*b*) occupation of p or d orbitals decreases ρ(0) as a result of screening the valence and core s orbitals from the nucleus.

As is known for the highly covalent gold complexes, Au$^{\mathrm{I}}$ whose gold hybrid orbitals (sp hybridization) have a larger s character than those of Au$^{\mathrm{III}}$ (dsp^2 hybridization) yield larger isomer shifts *i.e.* in terms of (*a*)]. From Figs. 1 and 2, it was found that i.s.$^{\mathrm{I}}$ is, on the contrary, smaller than i.s.$^{\mathrm{III}}$ for each mixed-valence compound. This behaviour can be explained in terms of (*b*) (Au$^{\mathrm{I}}$, 5d^{10}; Au$^{\mathrm{III}}$, 5d^{8}). The increase in i.s.$^{\mathrm{I}}$ from $\mathrm{Cs_2Au_2Cl_6}$ to $\mathrm{Cs_2Au_2I_6}$ is due to the increase in 6s population caused by increasing the σ-donor property of ligand halogens in $\mathrm{[Au^{I}X_2]^-}$ groups. The decrease in i.s.$^{\mathrm{III}}$ from $\mathrm{Cs_2Au_2Cl_6}$ to $\mathrm{Cs_2Au_2Br_6}$ is attributed mainly to the increase in $5d_{x^2-y^2}$ population [*i.e.* in terms of (*b*)], and the increase in i.s.$^{\mathrm{III}}$ from $\mathrm{Cs_2Au_2Br_6}$ to $\mathrm{Cs_2Au_2I_6}$ mainly to the increase in 6s population [*i.e.* in terms of (*a*)].

Cubic Phase of Bromo-bridged Complex.—Fig. 4 shows the spectrum of the cubic phase of the Cs–Au–Br system, $\mathrm{CsAu_{0.6}Br_{2.6}}$. In contrast to the tetragonal phase $\mathrm{Cs_2Au_2Br_6}$, only a single resonance line having a rather broad half-width was observed for the cubic phase. Strangely, the i.s. (1.52 mm s^{-1}) is larger than i.s.$^{\mathrm{III}}$ (1.12 mm s^{-1}) for the tetragonal phase and almost equal to i.s.$^{\mathrm{III}}$ (1.54 mm s^{-1}) for $\mathrm{Cs_2Au_2I_6}$. This suggests that the 6s population in the valence-shell molecular orbitals of Au in the cubic phase is larger than that in the corresponding orbitals of Au$^{\mathrm{III}}$ in the tetragonal phase. The observed half-width Γ (2.73 mm s^{-1}) is rather broader than that (2.34 mm s^{-1}) for gold foil (130 mg Au cm^{-2}). The rather broad line might be due to the bromine vacancies. In the system $\mathrm{CsAu_{0.6}Br_{2.6}}$ the gold and bromine vacancies are considered to be distributed in the lattice at random. Though most of the gold ions are six-co-ordinate, some are supposed to be five- or smaller co-ordination. In general, the oxidation state of gold ions with larger co-ordination number is higher. Therefore the valence state of six-co-ordinate gold would be +III, and that of five- or four-co-ordinate gold would be +II. Injected electrons reducing the gold(III) complex might be trapped at sites of five- or four-co-ordinate Au. Consequently, this system exhibits semiconducting behaviour, in spite of moving away from band half-filling by the non-stoichiometry. As mentioned above, the rather broad linewidth is considered to be due to the varieties of gold sites, and this implies that the oxidation state of Au is not completely homogeneous. The randomness of the gold and bromine vacancies would suppress the lattice distortion from cubic. We note that this spectrum resembles that (i.s. = 0.53 mm s^{-1} relative to gold in the ^{197}Pt source, q.s. = 0.94 mm s^{-1}, $\Gamma = 2.16$) reported by Gütlich *et al.*[10] for $Cs_{1.5}(Au^{II}{}^{I}Br_4)(Br_3)_{0.2}Br_{0.3}$, but the compositional ratio is different from that of our cubic phase $CsAu_{0.6}Br_{2.6}$.

Conclusion

Gold-197 Mössbauer spectra were measured to investigate the mixed-valence states of $Cs_2Au^IAu^{III}X_6$ (X = Cl, Br or I). The Au^I and Au^{III} were clearly distinguishable for all the compounds. In this three-dimensional mixed-valence system, as the charge-transfer interaction between Au^I and Au^{III} becomes stronger in the order $X = Cl < Br < I$ the quadrupole splitting of Au^{III} increases, while that of Au^I decreases from X = Cl to Br and does not change from X = Br to I. This behaviour suggests that the interaction between Au^I and Au^{III} should be stronger in the xy plane ($\perp$ c axis) than in the z direction ($\parallel$ c axis), and therefore two-dimensional correlation may be present in this mixed-valence system. For the cubic phase of the Cs–Au–Br system, $CsAu_{0.6}Br_{2.6}$, only a single resonance line having a rather broad half-width was observed. The cubic phase would be realized by the random distribution of bromine vacancies.

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