

P-T PHASE DIAGRAM AND GOLD VALENCE STATE OF NEW GOLD MIXED-VALENCE COMPLEXES, $\text{Cs}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{Y}_4]$ ($\text{X}, \text{Y} = \text{Cl}, \text{Br}, \text{I}; \text{X} \neq \text{Y}$)

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$\text{Cs}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{X}_4]$ ($\text{X} = \text{Cl}, \text{Br}, \text{and I}$) is well known for the perovskite-type gold mixed-valence system. This system undergoes pressure-induced and photo-induced Au valence transition from the mixed valence state of $\text{Au}^{\text{I/III}}$ to the single valence state of Au^{II} . Recently, we have succeeded in synthesizing new gold mixed-valence complexes having perovskite-type structure, $\text{Cs}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{Y}_4]$ ($\text{X}, \text{Y} = \text{halogen}, \text{X} \neq \text{Y}$), in organic solvent by using a new method. This hetero-halogen bridged gold mixed-valence system was confirmed by means of Raman spectroscopy. From the analysis of ^{197}Au Mössbauer spectra, it was elucidated that the charge transfer interaction between $\text{Au}^{\text{I}}(5d_{x^2-y^2})$ and $\text{Au}^{\text{III}}(5d_{x^2-y^2})$ in the a - b plane becomes dominant for the $\text{Au}^{\text{I}}\text{-Au}^{\text{III}}$ interaction in $\text{Cs}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{Y}_4]$ ($\text{X}, \text{Y} = \text{Cl}, \text{Br}, \text{and I}$) in the order of $\text{X} = \text{Cl} < \text{Br} < \text{I}$, where Y is fixed. In order to elucidate the Au valence transition for $\text{Cs}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{Y}_4]$, we have investigated the X-ray diffraction and Raman spectra under high pressure. Moreover, we have synthesized TLAuX_3 ($\text{X} = \text{Cl}$ and Br) having cubic perovskite structure and highly conducting behavior. The Au valence state in TLAuX_3 is considered to be Au^{II} at ambient pressure.

INTRODUCTION

Mixed-valence metal complexes are attracting current interest due to their characteristic physical properties [1, 2]. Among them, gold mixed-valence complexes, $\text{M}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{X}_4]$ ($\text{M} = \text{K}, \text{Rb}, \text{Cs}; \text{X} = \text{Cl}, \text{Br}, \text{and I}$) are well known for halogen-bridged gold mixed-valence complexes having perovskite-type structure (figure 1). In $\text{M}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{X}_4]$ ($\text{M} = \text{K}, \text{Rb}, \text{Cs}; \text{X} = \text{Cl}, \text{Br}, \text{and I}$), all the halogens are displaced from the midpoint between neighboring Au ions in the chains, and the linear $[\text{Au}^{\text{I}}\text{X}_2]^-$ - and square-planar $[\text{Au}^{\text{III}}\text{X}_4]^+$ - complexes are stacked alternately [3, 4]. Consequently, its structure consists of three-dimensional metal-halogen frameworks formed by elongated octahedra with Au^{III} and compressed octahedra with Au^{I} sharing their corners. Their characteristic properties of crystal structure and mixed valence state are quite similar to those of BaBiO_3 , which is the parent compound of the Cu-free superconductors, $\text{Ba}_{1-x}\text{KBiO}_3$ and $\text{BaBi}_{1-x}\text{PbO}_3$. The valence state of Bi has been considered to be a very important factor for its chemical and physical properties [5].

According to the classification of mixed valence system by Robin & Day [6], this mixed-valence system belongs to class II, in which strong inter-valence charge transfer (IVCT) band appears in the invisible region [7].

$\text{M}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{X}_4]$ ($\text{M} = \text{K}, \text{Rb}, \text{Cs}; \text{X} = \text{Cl}, \text{Br}, \text{and I}$) undergo the pressure-induced Au valence transition from the mixed valence state of $\text{Au}^{\text{I/III}}$ to the single valence state of Au^{II} [4, 8-9], which is coupled with a structural phase transition. In the case of $\text{Cs}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{X}_4]$ ($\text{X} = \text{Cl}, \text{Br}, \text{and I}$), the Au valence transition takes place at 11-12, 9, and 5.5 GPa, respectively [6]. In the pressure region below the Au valence transition, these complexes show a metallic behavior, which is presumably attributed to a dynamic two-electron exchange between the Au^{I} and Au^{III} states (i.e. highly mobile bipolarons) [4]. The metallic cubic phase appearing commonly for these complexes under high pressure and high temperature can be obtained as a metastable state even at ambient pressure and room temperature (r.t.) [4, 8]. Moreover, we have discovered a photo-induced Au valence transition for $\text{Cs}_2[\text{Au}^{\text{I}}\text{Br}_2][\text{Au}^{\text{III}}\text{Br}_4]$ [10].

These interesting phenomena strongly depend on the kind of the bridging halogen. For the sake of controlling the chemical bond, electronic state, and electron-phonon interaction for the halogen-bridged gold mixed-valence system, we have tried to control the bridging halogens in the a - b plane and along the c -axis,

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individually. Recently, we have succeeded in synthesizing hetero-halogen bridged gold mixed-valence complexes having perovskite-type structure, $\text{Cs}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{Y}_4]$ (X, Y = Cl, Br, and I; $\text{X} \neq \text{Y}$).

In this paper, we report the synthesis of the hetero-halogen bridged gold mixed-valence complexes, $\text{Cs}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{Y}_4]$ (X, Y = Cl, Br, and I), the crystal structure, the chemical bond, the gold valence state and the charge transfer interaction between Au^{I} and Au^{III} . Furthermore, we report the pressure induced gold valence transition from the mixed-valence state (Au^{I} , Au^{III}) to the single valence state (Au^{II}) for $\text{Cs}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{Y}_4]$ (X = Cl, Y = I). We also report TlAuX_3 (X = Cl and Br) having cubic perovskite structure and highly conducting behavior.

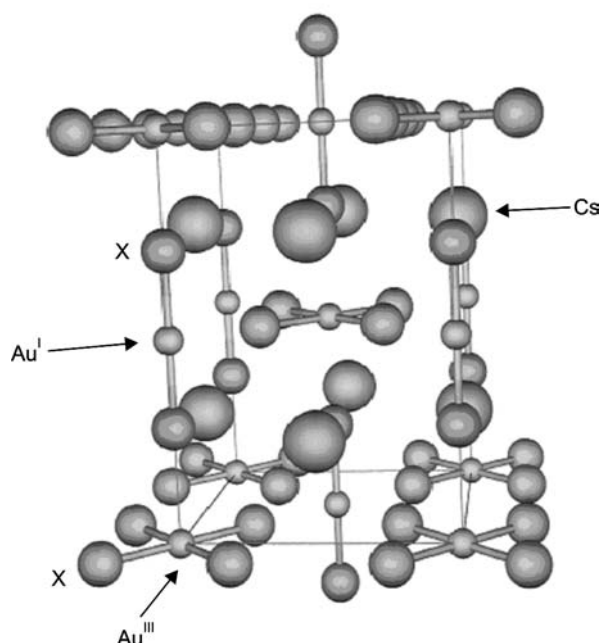


Figure 1. Crystal structure of $\text{Cs}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{Y}_4]$ (X = Cl, Br, and I).

EXPERIMENTAL

$\text{Cs}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{Y}_4]$ (X, Y = Cl, Br, and I) was prepared in the following way. Solutions of $(\text{C}_4\text{H}_9)_4\text{N}[\text{Au}^{\text{I}}\text{X}_2]$ and $(\text{C}_4\text{H}_9)_4\text{N}[\text{Au}^{\text{III}}\text{Y}_4]$ in 1,1,2-trichloroethane were stirred at -20°C , individually. A solution of $\text{C}_6\text{H}_5\text{SO}_3\text{Cs}$ in methanol was stirred at -20°C . To this, the solutions of $(\text{C}_4\text{H}_9)_4\text{N}[\text{Au}^{\text{I}}\text{X}_2]$ and $(\text{C}_4\text{H}_9)_4\text{N}[\text{Au}^{\text{III}}\text{Y}_4]$ in 1,1,2-trichloroethane were added and stirred at -20°C for 1 hr. In this way, $\text{Cs}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{Y}_4]$ (X, Y = Cl, Br, and I) was obtained as black colored precipitate. In the case of $\text{Cs}_2[\text{Au}^{\text{I}}\text{Cl}_2][\text{Au}^{\text{III}}\text{I}_4]$, these temperatures were kept at -10°C . For TlAuX_3 , the solutions of $(\text{C}_4\text{H}_9)_4$

$\text{N}[\text{Au}^{\text{I}}\text{X}_2]$ and $(\text{C}_4\text{H}_9)_4\text{N}[\text{Au}^{\text{III}}\text{Y}_4]$ in 1,1,2-trichloroethane were added to a solution of HCOOTl in methanol. Then it was stirred at room temperature until the solution becomes colorless transparent.

The single crystal X-ray analysis was carried out by using a RIGAKU RAXIS-RAPID Imaging Plate diffractometer equipped with graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.071069 \text{ nm}$) at 23°C . For the high pressure powder X-ray analysis, a diamond anvil cell with mixed liquid, FC70:FC77 = 1:1, as a pressure medium was used. The applied pressure was monitored using the luminescence peak of a small piece of ruby placed in the gasket hole.

Raman spectroscopic measurement was carried out using an argon ion laser (514.5 nm) in a backward configuration.

A Mössbauer spectroscopic measurement of the 77.34 keV transition in ^{197}Au was performed with both source and absorber cooled down to 16 K by using a constant-acceleration spectrometer with a NaI scintillation counter. A ^{197}Pt source was obtained by neutron irradiation of 98 % enriched ^{196}Pt metal by the nuclear reaction $^{196}\text{Pt}(n,\lambda)^{197}\text{Pt}$ in the Kyoto University Reactor. The observed spectra were analyzed by fitting with Lorentzian curves.

RESULTS AND DISCUSSION

The crystal structure of $\text{Cs}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{Y}_4]$ is distorted perovskite-type. In the crystal, all the halogens are displaced from the midpoint between neighboring Au ions in the chains, and the linear $[\text{Au}^{\text{I}}\text{X}_2]^-$ and square-planar $[\text{Au}^{\text{III}}\text{Y}_4]^-$ complexes are stacking alternately. There are two relative orientations between $[\text{Au}^{\text{I}}\text{X}_2]^-$ and $[\text{Au}^{\text{III}}\text{Y}_4]^-$ (figure 2). In one, the $\cdots \text{X} - \text{Au}^{\text{I}} - \text{X} \cdots \text{Au}^{\text{III}} \cdots \text{X} - \text{Au}^{\text{I}} - \text{X} \cdots$ network lies

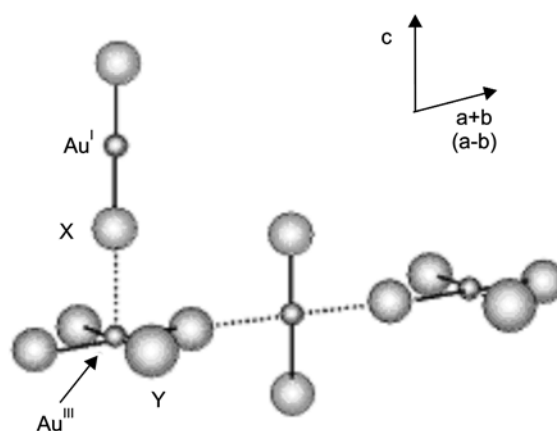


Figure 2. Two relative orientations between linear $[\text{Au}^{\text{I}}\text{X}_2]^-$ and square-planar $[\text{Au}^{\text{III}}\text{Y}_4]^-$.

along the c -axis, while, the $\cdots Y - Au^{III} - Y \cdots Au^I \cdots Y - Au^{III} - Y \cdots$ network lies in the ab plane. Consequently, its structure consists of three-dimensional metal-halogen frame-works forming elongated octahedra with Au^{III} and compressed octahedra with Au^I sharing their corners.

In order to confirm the ideal structure of $Cs_2[Au^I I_2][Au^{III} Br_4]$, we have investigated the Raman spectra for the single crystals of $Cs_2[Au^I I_2][Au^{III} Br_4]$, $Cs_2[Au^I Br_2][Au^{III} Br_4]$, and $(C_4H_9)_4N [Au^I I_2]$ [11]. In the case of $Cs_2[Au^I Br_2][Au^{III} Br_4]$, two A_{1g} mode are observed in the $c(a+b, a+b)c$ configuration, while one B_{1g} mode is observed in the $c(a+b, a-b)c$ configuration. The lower-lying two modes, i.e. $B_{1g}(178\text{ cm}^{-1})$ and $A_{1g}(179\text{ cm}^{-1})$ modes correspond to the stretching modes of the $[Au^{III} Br_4]^-$ molecule, while the higher-lying $A_{1g}(220\text{ cm}^{-1})$ mode corresponds to that of the $[Au^I Br_2]$ molecule. For $Cs_2[Au^I I_2][Au^{III} Br_4]$, the $A_{1g}(220\text{ cm}^{-1})$ mode corresponding to the $[Au^I Br_2]$ molecule disappears. Instead, the Raman spectrum corresponding to the $[Au^I I_2]$ molecule appears at about 150 cm^{-1} . In this way, it is proved that the hetero-halogen bridged gold mixed-valence complex, $Cs_2[Au^I I_2][Au^{III} Br_4]$, is formed.

Figure 3 shows the ^{197}Au Mössbauer spectra for $Cs_2[Au^I Cl_2][Au^{III} Y_4]$ ($Y = Cl, Br, \text{ and } I$). The ^{197}Au Mössbauer parameters of isomer shift (δ), quadrupole splitting (Δ), full width of half maximum (Γ), and the intensity ratio [$I(Au^I)/I(Au^{III})$] are given in table 1. δ -values are referred to gold foil. A best fit is obtained with two doublets, the outer doublet with lower intensity being assigned to Au^I , and the inner to Au^{III} . These assignments have resemblance to those previously reported for $Cs_2Au_2X_6$. Figure 4 shows the isomer shift and quadrupole splitting for $Cs_2[Au^I Cl_2][Au^{III} Y_4]$ ($Y = Cl, Br, \text{ and } I$).

^{197}Au Mössbauer spectroscopy is the most powerful method to investigate the valence state and the electronic state for mixed valence gold complexes. In $Cs_2[Au^I X_2][Au^{III} Y_4]$, there are two types of charge transfer interac-

tion between Au^I and Au^{III} . One is the charge transfer interaction between $Au^I(5d_{x^2})$ and $Au^{III}(5d_{x^2-y^2})$. The other is that between $Au^I(5d_{x^2-y^2})$ and $Au^{III}(5d_{x^2-y^2})$. According to MO calculations for $Cs_2[Au^I X_2][Au^{III} X_4]$ ($X = Cl, Br, \text{ and } I$) [4], the $Au^I(5d_{x^2})$ orbital of $[Au^I X_2]$ consists of $6s$ component because of ds hybridization. However, the $Au^I(5d_{x^2-y^2})$ orbital of $[Au^I X_2]$ does not consist of $6s$ component. Therefore, if the charge transfer interaction between $Au^I(5d_{x^2})$ and $Au^{III}(5d_{x^2-y^2})$ is predominant, the isomer shift of Au^I becomes small, because the s -electron population at the Au^I site decreases due to the charge transfer from Au^I to Au^{III} . On the other hand, if the charge transfer interaction between $Au^I(5d_{x^2-y^2})$ and $Au^{III}(5d_{x^2-y^2})$ is predominant, the isomer shift of Au^I becomes large because of the decrease in the screening.

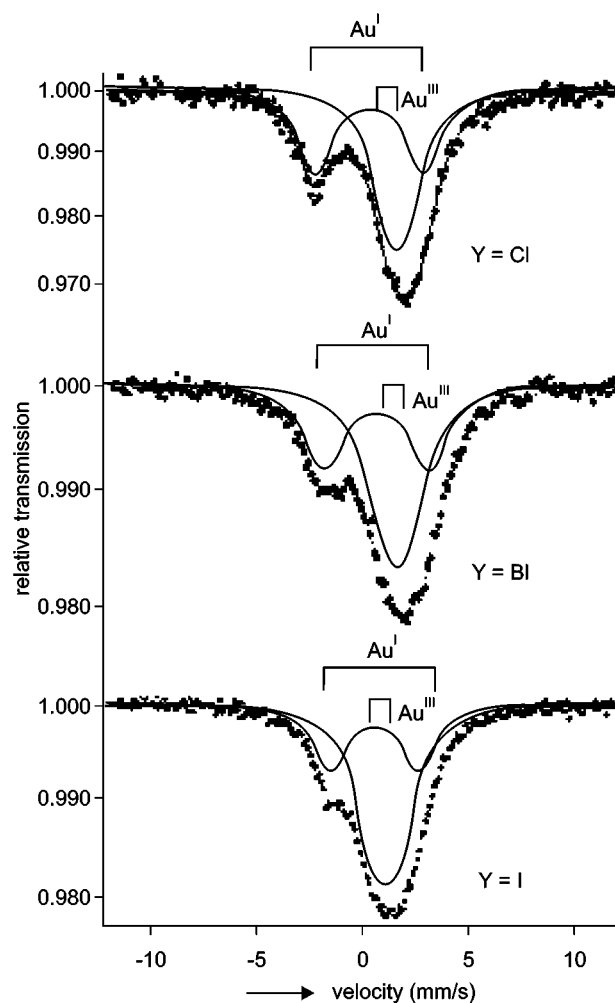


Figure 3. ^{197}Au Mössbauer spectra for $Cs_2[Au^I Cl_2][Au^{III} Y_4]$ ($Y = Cl, Br \text{ and } I$). $T = 16\text{ K}$.

Table 1. ^{197}Au Mössbauer parameters for $Cs_2[Au^I Cl_2][Au^{III} Y_4]$ ($Y = Cl, Br, I$). δ (mm/s): isomer shift relative to metallic gold, Δ (mm/s): quadrupole splitting, Γ (mm/s): full width at half maximum, $I(Au^I)/I(Au^{III})$: intensity ratio.

	site	δ	Δ	Γ	$I(Au^I)/I(Au^{III})$
		(mm/s)			
$Cs_2[Au^I Cl_2][Au^{III} Cl_4]$	Au^I	0.20	5.06	2.04	0.820
	Au^{III}	1.55	0.76	2.14	
$Cs_2[Au^I Cl_2][Au^{III} Br_4]$	Au^I	0.47	4.89	2.33	0.753
	Au^{III}	1.39	1.08	2.33	
$Cs_2[Au^I Cl_2][Au^{III} I_4]$	Au^I	0.50	4.97	2.36	0.574
	Au^{III}	1.14	1.42	2.36	

As shown in figure 4, IS of Au^{I} in $\text{Cs}_2[\text{Au}^{\text{I}}\text{Cl}_2][\text{Au}^{\text{III}}\text{Y}_4]$ increases in the order of $\text{Y} = \text{Cl} < \text{Br}$, which implies that the charge transfer interaction between $\text{Au}^{\text{I}}(5d_{x^2-y^2})$ and $\text{Au}^{\text{III}}(5d_{x^2-y^2})$ becomes strong in the order of $\text{Y} = \text{Cl} < \text{Br}$. On the other hand, IS of Au^{I} in $\text{Cs}_2[\text{Au}^{\text{I}}\text{Cl}_2][\text{Au}^{\text{III}}\text{I}_4]$ is quite similar to that of Au^{I} in $\text{Cs}_2[\text{Au}^{\text{I}}\text{Cl}_2][\text{Au}^{\text{III}}\text{Br}_4]$, while the difference of IS between Au^{I} and Au^{III} in $\text{Cs}_2[\text{Au}^{\text{I}}\text{Cl}_2][\text{Au}^{\text{III}}\text{I}_4]$ is quite smaller than that in $\text{Cs}_2[\text{Au}^{\text{I}}\text{Cl}_2][\text{Au}^{\text{III}}\text{Br}_4]$. From these results, it is concluded that the charge transfer interaction between Au^{I} and Au^{III} in $\text{Cs}_2[\text{Au}^{\text{I}}\text{Cl}_2][\text{Au}^{\text{III}}\text{Y}_4]$ ($\text{Y} = \text{Cl}, \text{Br}, \text{I}$) is strongest when $\text{Y} = \text{I}$, i.e. in $\text{Cs}_2[\text{Au}^{\text{I}}\text{Cl}_2][\text{Au}^{\text{III}}\text{I}_4]$ and not only the charge transfer interaction between $\text{Au}^{\text{I}}(5d_{x^2-y^2})$ and $\text{Au}^{\text{III}}(5d_{x^2-y^2})$ but also that between $\text{Au}^{\text{I}}(5d_{x^2-y^2})$ and $\text{Au}^{\text{III}}(5d_{x^2-y^2})$ is predominant in $\text{Cs}_2[\text{Au}^{\text{I}}\text{Cl}_2][\text{Au}^{\text{III}}\text{I}_4]$.

The intensity ratio of the two components, $I(\text{Au}^{\text{I}})/I(\text{Au}^{\text{III}})$ should be 1:1 because of the $\text{Au}^{\text{I}}/\text{Au}^{\text{III}}$ compositional ratio in stoichiometric $\text{Cs}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{Y}_4]$. However, the experimental ratios are smaller than the expected ones. The unequal intensities are due to the difference in recoil-free fractions $f(\text{Au}^{\text{I}})$ and $f(\text{Au}^{\text{III}})$ for the Au^{I} and Au^{III} sites in $\text{Cs}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{Y}_4]$.

Since the Au^{I} is in two-fold (linear) ligand coordination and the Au^{III} is in four-fold (square-planar) coordination, the environment of the Au^{III} in $\text{Cs}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{X}_4]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), is more rigid than that of the Au^{I} . Therefore, the mean square vibrational amplitude of Au^{III} is considered to be smaller than that of Au^{I} . According to data for $\text{Cs}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{X}_4]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), the intensity ratio $I(\text{Au}^{\text{I}})/I(\text{Au}^{\text{III}})$ should be around 0.8 under 16 K. This value is in good agreement with the theoretical value which is calculated with isotropic temperature factors $I(\text{Au}^{\text{I}})/I(\text{Au}^{\text{III}})$ obtained by XRD measurement. On the other hand, for $\text{Cs}_2[\text{Au}^{\text{I}}\text{Cl}_2][\text{Au}^{\text{III}}\text{I}_4]$ and $\text{Cs}_2[\text{Au}^{\text{I}}\text{I}_2][\text{Au}^{\text{III}}\text{I}_4]$ are 0.574 and 1.26, respectively. The results indicate that the recoil-free fraction of $[\text{Au}^{\text{I}}\text{I}_2]^-$ and $[\text{Au}^{\text{III}}\text{I}_4]^-$ are larger than those of $[\text{Au}^{\text{I}}\text{Cl}_2]^-$ and $[\text{Au}^{\text{III}}\text{Cl}_4]^-$. Therefore, in the case of $\text{Cs}_2[\text{Au}^{\text{I}}\text{I}_2][\text{Au}^{\text{III}}\text{I}_4]$, the recoil-free fraction, $f(\text{Au}^{\text{I}})$, for the Au^{I} site in two-fold ligand coordination is larger than that for the Au^{III} site in four-fold coordination.

Pressure dependence of powder XRD pattern for $\text{Cs}_2[\text{Au}^{\text{I}}\text{Cl}_2][\text{Au}^{\text{III}}\text{I}_4]$ at room temperature is shown in figure 5.

Figure 6 shows the pressure dependence of the (103) and (211) reflections due to the super structure caused by the displacement of the halogen ions from the midpoint between the Au^{I} and Au^{III} ions. As seen in figure 5, the intensities of the (103) and (211) reflections decrease with increasing pressure, which implies that the bridging halogen ions approach the midpoint of the Au^{I} and Au^{III} ions with increasing pressure. In the pressure region between 6 GPa and 7 GPa, the (103) and (211) reflections completely disappear. Therefore, it is concluded that the bridging halogens are located at the midpoint between neighboring Au ions and the single valence state of Au^{II} is observed above 7 GPa. This behavior is consistent with that of $\text{Cs}_2\text{Au}_2\text{I}_6$ which shows a tetragonal to tetragonal phase transition accompanied with the gold valence transition from the mixed-valence state of $\text{Au}^{\text{I,III}}$ to the single-valence state of Au^{II} [8]. In this way, we obtained the phase diagram of $\text{Cs}_2[\text{Au}^{\text{I}}\text{Cl}_2][\text{Au}^{\text{III}}\text{I}_4]$. Figure 7 shows the phase diagrams for $\text{Cs}_2[\text{Au}^{\text{I}}\text{Cl}_2][\text{Au}^{\text{III}}\text{Cl}_4]$, $\text{Cs}_2[\text{Au}^{\text{I}}\text{Cl}_2][\text{Au}^{\text{III}}\text{I}_4]$, and $\text{Cs}_2[\text{Au}^{\text{I}}\text{I}_2][\text{Au}^{\text{III}}\text{I}_4]$, where T and C denote tetragonal phase and cubic phase, respectively.

As seen in figure 7, the critical pressure at which the valence transition from the mixed valence state of $\text{Au}^{\text{I,III}}$ to the single valence state of Au^{II} occurs for $\text{Cs}_2[\text{Au}^{\text{I}}\text{Cl}_2][\text{Au}^{\text{III}}\text{I}_4]$ is very close to that for $\text{Cs}_2[\text{Au}^{\text{I}}\text{I}_2][\text{Au}^{\text{III}}\text{I}_4]$. This implies that the interaction between Au^{I} and Au^{III} responsible for controlling the pressure-induced gold valence transition in $\text{Cs}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{Y}_4]$ is the charge transfer interaction between Au^{I} and Au^{III} through the bridging halogen, Y, in the *a-b* plane.

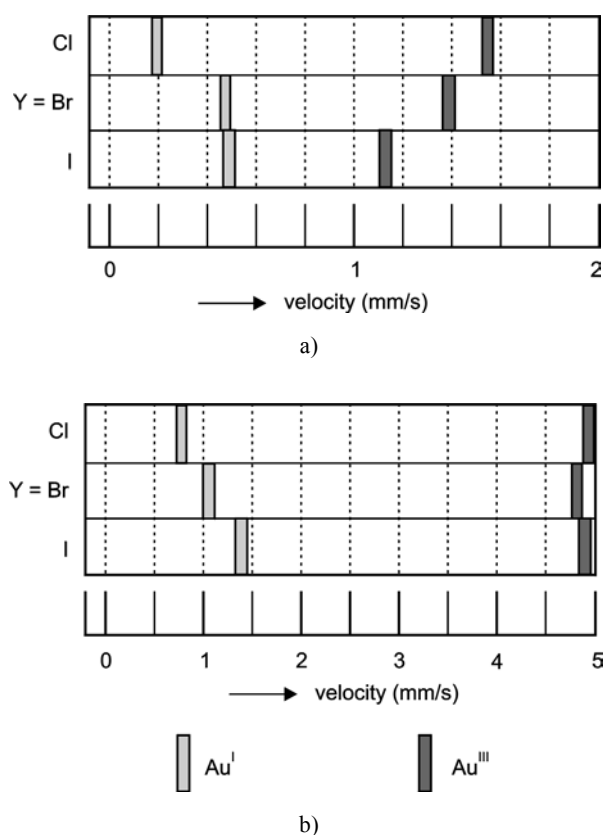


Figure 4. Isomer shifts (a) and Quadrupole splittings (b) of Au^{I} and Au^{III} for $\text{Cs}_2[\text{Au}^{\text{I}}\text{Cl}_2][\text{Au}^{\text{III}}\text{Y}_4]$ ($\text{Y} = \text{Cl}, \text{Br}, \text{I}$).

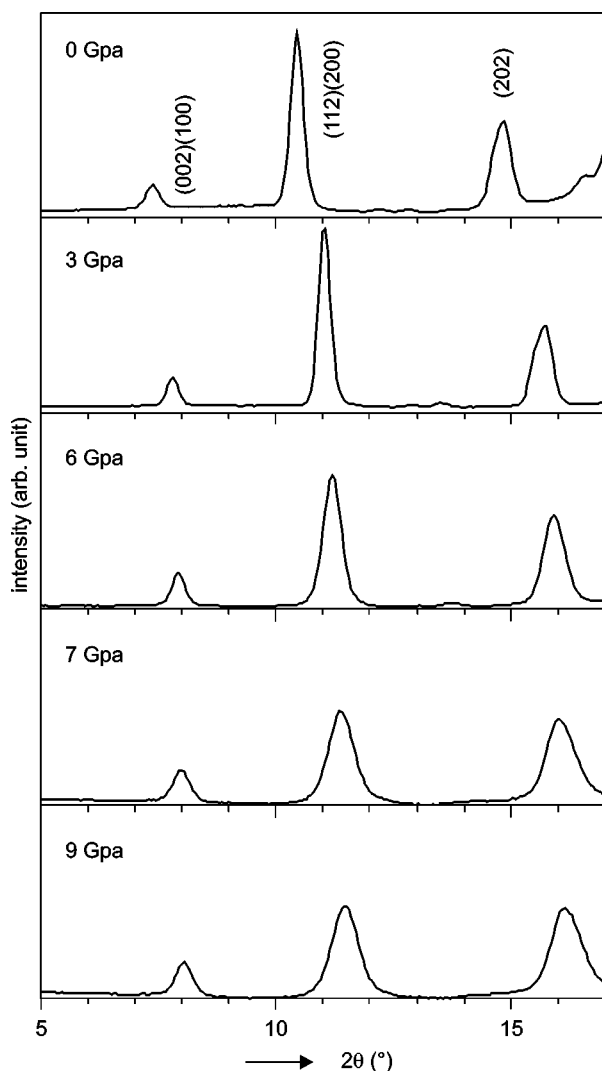


Figure 5. Pressure dependence of the powder XRD pattern of $Cs_2[Au^I Cl_2][Au^{III} I_4]$ at r.t.

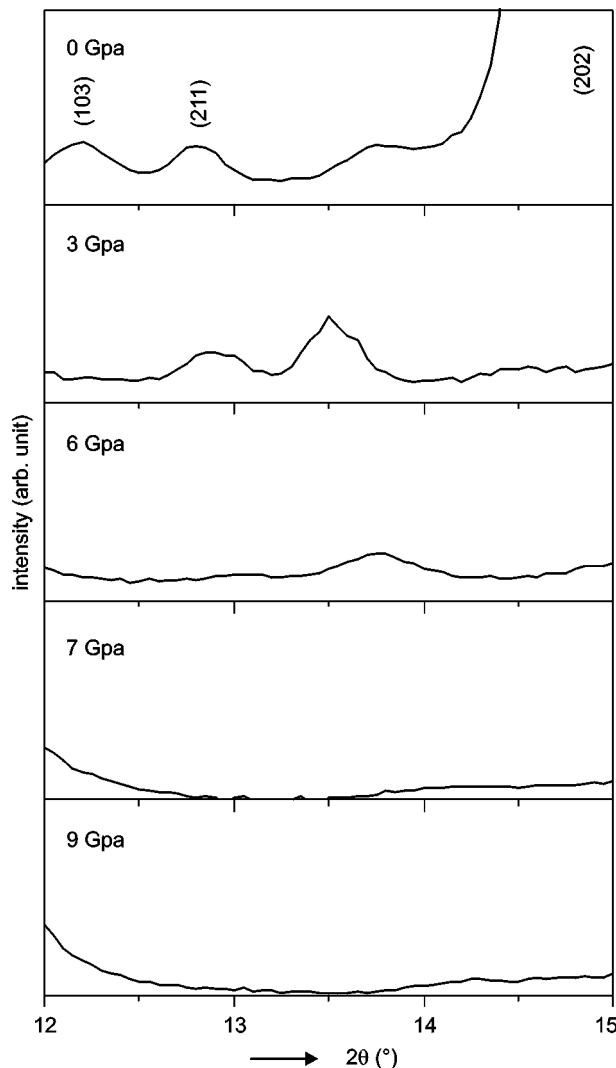


Figure 6. Pressure dependence of the (103) and (211) reflections of $Cs_2[Au^I Cl_2][Au^{III} I_4]$ at r.t.

In the case of $Cs_2[Au^IX_2][Au^{III}X_4]$ ($X = Cl, Br$ and I), the cubic perovskite structure with single valence state of Au^I appears under high pressure and high temperature [4]. Recently, we have obtained $TlAuX_3$ ($X = Cl$ and Br) having cubic perovskite structure at ambient pressure and room temperature, by a synthesis route similar to that of $Cs_2[Au^IX_2][Au^{III}Y_4]$.

The lattice constants, a_{cubic} , are 3.82 and 3.96 Å for $X = Cl$ and Br , respectively, while the cubic phase of $Cs_2[Au^I Cl_2][Au^{III} Cl_4]$ has the lattice constant of $a_{cubic} = 4.7$ Å at 18 GPa. In the case of $TlAuX_3$, the lattice constant is quite shorter than that of the cubic $Cs_2[Au^I Cl_2][Au^{III} Cl_4]$ under high pressure, which suggests the existence of strong $Au-Tl$ bonding due to the mixing between the filled 6s band of Tl^I and the empty 6s band of Au^I . In the cases of $Cs_2[Au^IX_2][Au^{III}X_4]$ ($X = Cl, Br$, and I), the cubic perovskite structure having metallic conductivity is found under high pressure and high temperature [8],

while the same type of phase is obtained even at ambient pressure for $TlAuX_3$ ($X = Cl$ and Br). The Au valence state in $TlAuX_3$ is considered to be Au^I at ambient pressure.

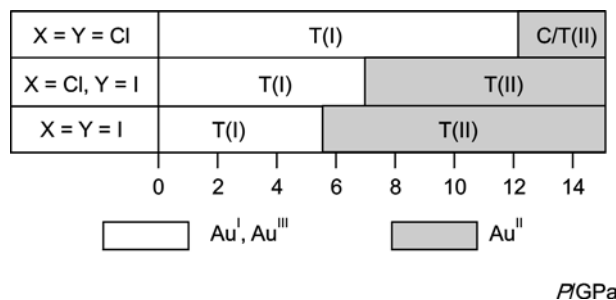


Figure 7. Phase diagram of $Cs_2[Au^IX_2][Au^{III}Y_4]$ ($X, Y = Cl, Br, I$) at r.t. T: tetragonal phase, C: cubic phase.

CONCLUSIONS

We have synthesized new gold mixed-valence complexes having perovskite-type structure, $\text{Cs}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{Y}_4]$ (X, Y = halogen, $\text{X} \neq \text{Y}$), in organic solvent by using a new method. The main results obtained from Raman spectroscopy, X-ray structural analysis under high pressure and ^{197}Au Mössbauer spectroscopy are summarized as follows.

- 1) The hetero-halogen bridged gold mixed-valence system, $\text{Cs}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{Y}_4]$, was confirmed by means of Raman spectroscopy.
- 2) From the analysis of ^{197}Au Mössbauer spectra, it was elucidated that the charge transfer interaction between $\text{Au}^{\text{I}}(5d_{x^2-y^2})$ and $\text{Au}^{\text{III}}(5d_{x^2-y^2})$ in the *a-b* plane is dominant for the $\text{Au}^{\text{I}}\text{-Au}^{\text{III}}$ interaction in $\text{Cs}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{Y}_4]$ (X, Y = Cl, Br, and I).
- 3) The charge transfer interaction between Au^{I} and Au^{III} in $\text{Cs}_2[\text{Au}^{\text{I}}\text{Cl}_2][\text{Au}^{\text{III}}\text{Y}_4]$ (Y = Cl, Br, I) is strongest when $\text{Y}=\text{I}$, i.e. in $\text{Cs}_2[\text{Au}^{\text{I}}\text{Cl}_2][\text{Au}^{\text{III}}\text{I}_4]$ and not only the charge transfer interaction between $\text{Au}^{\text{I}}(5d_{x^2-y^2})$ and $\text{Au}^{\text{III}}(5d_{x^2-y^2})$ but also that between $\text{Au}^{\text{I}}(5d_{x^2})$ and $\text{Au}^{\text{III}}(5d_{x^2-y^2})$ is predominant in $\text{Cs}_2[\text{Au}^{\text{I}}\text{Cl}_2][\text{Au}^{\text{III}}\text{I}_4]$.
- 4) The interaction between Au^{I} and Au^{III} responsible for controlling the pressure-induced gold valence transition in $\text{Cs}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{Y}_4]$ is the charge transfer interaction between Au^{I} and Au^{III} through the bridging halogen, Y, in the *a-b* plane.
- 5) We have synthesized TlAuX_3 (X = Cl and Br) having cubic perovskite structure and highly conducting behavior. The Au valence state in TlAuX_3 is considered to be Au^{II} at ambient pressure.

The preparation of $\text{Cs}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{Y}_4]$ (X, Y = Cl, Br, and I; $\text{X} \neq \text{Y}$) allows us to get a grip on controlling the electron-phonon interaction, chemical bonding, and charge transfer interaction in gold mixed valence system. Furthermore, by using a method similar to the synthesis procedure of $\text{Cs}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{Y}_4]$, it is possible to synthesize not only halogen-bridged gold mixed valence complexes but also pseudo-halogen bridged complexes or hetero-transition metal complexes.

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P-T FÁZOVÝ DIAGRAM A VALENCE ZLATA
V NOVÝCH KOMPLEXECH $\text{Cs}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{Y}_4]$ (X, Y = Cl,
Br, I; $\text{X} \neq \text{Y}$) S Au VE DVOU VALENČNÍCH STAVECH

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$\text{Cs}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{Y}_4]$ (X = Cl, Br, a I) je známý komplex zlata s ionty Au ve dvou mocenstvích a se strukturou perovskitu. Tento systém podléhá vlivem tlaku nebo ozáření změně mocenství Au ze směsného stavu $\text{Au}^{\text{I/III}}$ na stav s jedinou valencí Au^{II} . V poslední době jsme úspěšně syntetizovali nové Au komplexy se smíšenou valencí s perovskitovou strukturou, $\text{Cs}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{Y}_4]$ (X, Y = halogen, $\text{X} \neq \text{Y}$) v organickém rozpouštědle s použitím nové metody. Vznik vícevalentního Au komplexu s halogenovými můstky byl potvrzen Ramanovou spektroskopií. Analýzou ^{197}Au Mössbauerových spekter bylo zjištěno, že interakce přenosu náboje mezi $\text{Au}^{\text{I}}(5d_{x^2-y^2})$ a $\text{Au}^{\text{III}}(5d_{x^2-y^2})$ v rovině *a-b* se stává převládající pro $\text{Au}^{\text{I}}\text{-Au}^{\text{III}}$ interakce v $\text{Cs}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{Y}_4]$ (X, Y = Cl, Br, a I) v pořadí $\text{X} = \text{Cl} < \text{Br} < \text{I}$, kde Y se nemění. Abychom objasnili valenční přechod v $\text{Cs}_2[\text{Au}^{\text{I}}\text{X}_2][\text{Au}^{\text{III}}\text{Y}_4]$, provedli jsme rtg difrakci a Ramanovu spektroskopii za vysokého tlaku. Dále jsme syntetizovali TlAuX_3 (X = Cl a Br) s mřížkou kubického perovskitu a s vysokou vodivostí. Au v TlAuX_3 se považuje za dvojmocné za normálního tlaku.