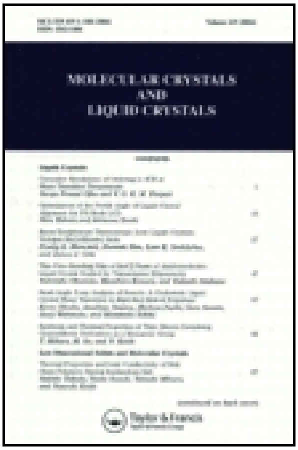

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Studies of Mixed—Valence States in One Dimentional Halogen-Bridged Gold Compounds [Au^{I}X(DBS)][Au^{III}X$_3$(DBS)](X=Cl, Br, I: dbs=dibenzylsulfide)

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Studies of Mixed -Valence States in One Dimentional Halogen-Bridged Gold Compounds $[Au^{I}X(DBS)][Au^{III}X_3(DBS)]$(X=Cl, Br, I : dbs=dibenzylsulfide)

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We have investigated the crystal structure and the Au valence states in $[Au^{I}X(DBS)][Au^{III}X_3(DBS)]$ (X=Cl, Br, I). From the analysis of ^{197}Au Mössbauer spectra in $AuCl_x(DBS)$ (X=1, 2, 3), it is proved that $AuCl_2(DBS)$ has a mixed-valence state of Au^{I} and Au^{III}. Comparing with the isomer shifts of Au^{I} and Au^{III}in $Cs_2[Au^{I}Cl_2][Au^{III}Cl_4]$, it is considered that the charge transfer interaction between Au^{I} and Au^{III} in $AuCl_2(DBS)$ is smaller than that in $Cs_2[Au^{I}Cl_2][Au^{III}Cl_4]$. The isomer shifts of Au^{I} and Au^{III} in $AuCl_2(DBS)$ are much larger than those in $Cs_2[Au^{I}Cl_2][Au^{III}Cl_4]$, which should be attributed to the highly covalent bond between Au and S. From the ESR spectra, it is shown that the Au^{II} states exist as the mismatch of the valence alternation in $AuCl_2(DBS)$. The half-field ESR signal for $\Delta M=\pm 2$ at low temperature indicates the dimerization of the Au^{II} state with ferromagnetic exchange interaction. Also, the X-ray powder patterns of $AuX_2(DBS)$ (X=Cl, Br) shows these two complexes to be isomorphous.

Keywords: mixed-valence; MX chain; two-leg ladder; ^{197}Au Mössbauer spectroscopy; charge transfer interaction

INTRODUCTION

Halogen bridged Pt mixed-valence complexes have been studied from the viewpoint of one-dimentional system having strong electron-phonon interaction and of the non-linear excitations such as solitons and polarons. [Au^{I}Cl(DBS)][Au^{III}Cl$_3$(DBS)] is one of a few number of halogen-bridged linear chain complexes involving gold. According to a single crystal X-ray analysis[1], [Au^{I}Cl(DBS)][Au^{III}Cl$_3$(DBS)] consists of alternating Au^{I}Cl(DBS) and Au^{III}Cl$_3$(DBS) units in a neutral chain, which is shown in Fig.1. The $\cdot\cdot$ Au^{I} $\cdot\cdot$ Cl ——Au^{III}——Cl $\cdot\cdot$ Au^{I} $\cdot\cdot$ network along the chain axis in [Au^{I}Cl(DBS)][Au^{III}Cl$_3$(DBS)] is quite similar to that lying the a-b plane in the three-dimensional mixed valence complex, Cs$_2$[Au^{I}Cl$_2$][Au^{III}Cl$_4$][2]. Moreover, this crystal structure shows the paring of two one-dimentional chains, i.e., two-leg ladder. Recently, there have been increasing interests in spin-ladder systems because of unique magnetic properties of (VO)$_2$P$_2$O$_7$[3] and the superconductivity of Sr$_{0.4}$Ca$_{13.6}$Cu$_{24}$O$_{41.84}$[4] realized by carrier-dopping. We expect to control the Au valence states, solitons and polarons by doping holes into the two-leg ladder Au-X chains as well as polyacetylene. From an interest in the above mentioned viewpoints, we have systematically investigated the crystal structure and Au valence states in [Au^{I}X(DBS)][Au^{III}X$_3$(DBS)] (X=Cl, Br, I) by means of X-ray structural analysis, ^{197}Au Mössbauer spectroscopy and ESR measurement.

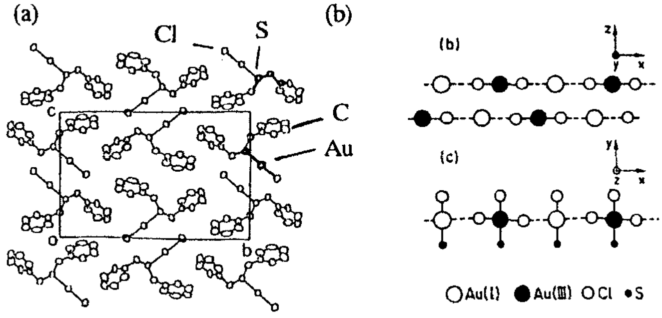

Figure 1 (a) Crystal structure of AuCl$_2$(DBS) [1] and (b) Schematic two-leg ladder structure of Au-Cl chain[5].

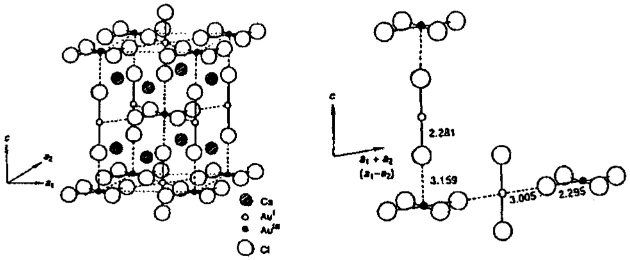

Figure 2 Crystal Structure of $Cs_2[Au^{I}Cl_2][Au^{III}Cl_4]$ [2]

EXPERIMENTAL

Sample Preparation

$AuCl_X(DBS)(X=1,2,3)$ and $AuBr_2(DBS)$ were prepared according to ref[6, 7, 8].

Mössbauer Spectroscopic Measurement

Mössbauer spectroscopic measurements of the 77.34 keV transition in ^{197}Au were carried out with both source and absorber cooled down to 16 K using a constant-acceleration spectrometer with a NaI (Tl) scintillation counter. A ^{197}Pt source was obtained by neutron irradiation of 98 % enriched platinum due to the nuclear reaction $^{196}Pt[n,\gamma]^{197}Pt$ in the Kyoto University Reactor (KUR).

ESR Measurement

The ESR spectra of $AuCl_2(DBS)$ were measured from 4.2 K to room temperature with an X-band JES-TE300 spectrometer. The sample was irradiated by a Xe-lamp through a window of the cavity keeping low temperature.

RESULTS AND DISSCUSSION

Figure 3 shows the ^{197}Au Mössbauer spectra of powdered AuCl(DBS), $AuCl_2(DBS)$, and $AuCl_3(DBS)$. A best fit of $AuCl_2(DBS)$ in Fig.3 is obtained with two doublets, the outer with lower intensity being assigned to Au^{I}, the inner to Au^{III}. In this complex, the Au^{I} site is in two (linear) ligand coordination and the Au^{III} one is in four-fold (square planar) ligand coordination. So that, the environment of Au^{III} site is more rigid than that of Au^{I} site, which is responsible for that the intensity ratio, I (Au^{I}/ Au^{III}), is remarkably deviated from 1.0.

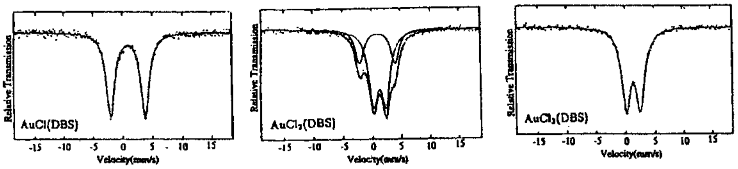

Figure 3 ^{197}Au Mössbauer spectra of AuCl(DBS), AuCl2(DBS), and AuCl3(DBS) at 16K. Relative to gold in platinum.

Table 1 shows the isomer shifts of AuCl$_X$(DBS)(X=1, 2, 3), Cs$_2$[Au^{I}Cl$_2$][Au^{III}Cl$_4$], and its two constituent complexes, [Bu$_4$N][AuClx](X=2, 4). The isomer shifts of Au^{I} and Au^{III} in Cs$_2$[Au^{I}Cl$_2$][Au^{III}Cl$_4$] are quite different from those of Au^{I} and Au^{III} in its constituent complexes. On the other hand, the isomer shifts of Au^{I} and Au^{III} in AuCl$_2$(DBS) are slightly different from those of Au^{I} in Au^{I}Cl(DBS) and Au^{III} in AuCl$_3$(DBS), respectively. The fact shows that the charge transfer interaction of AuCl$_2$(DBS) is much smaller than that of Cs$_2$[Au^{I}Cl$_2$][Au^{III}Cl$_4$]. One reason for it is that the Au^{I}- Au^{III} bond of AuCl$_2$(DBS) is longer by 0.39 Å than that of Cs$_2$[Au^{I}Cl$_2$][Au^{III}Cl$_4$]. The isomer shifts of Au^{I} and Au^{III} in AuCl$_2$(DBS) are much larger than those of Au^{I} and Au^{III} in Cs$_2$[Au^{I}Cl$_2$][Au^{III}Cl$_4$], which should be attributed to the highly covalent bond between Au and S. As is known for highly covalent gold complexes, Au orbitals have a large 6s character. In fact, from our EHMO calculation, the populations of 6s orbital of Au^{I} and Au^{III} in AuCl$_2$(DBS) are estimated at 0.45 and 0.32, respectively. On the other hand, the populations of 6s orbital of Au^{I} and Au^{III} in Cs$_2$[Au^{I}Cl$_2$][Au^{III}Cl$_4$] are estimated at 0.35 and 0.30, respectively.

Figure 4 shows the temperature dependence of the ESR spectra of $AuCl_2$(DBS). The spectra of $AuCl_2$(DBS) begin to arise at about 80 K and the intensity gradually increases with decreasing temperature. This signal coresponds to the $\mathrm{Au^{II}}$ states introduced into the Au-Cl chains during the crystal growth. The half-field ESR signal for $\Delta M = \pm 2$ transition appearing at about 150 mT below 20 K indicates the existence of the dimerized $\mathrm{Au^{II}}$ states. It is not clear whether the dominant exchange interaction is the intra-chain interaction or the inter-chain one. Since the half-field ESR signal for the $\Delta M = \pm 2$ transition increases with decreasing temperature, it is considered that the exchange interaction between $\mathrm{Au^{II}}$ site is ferromagnetic. The photoinduced effect on the ESR signal of $AuCl_2$(DBS) has not been observed.

	$\mathrm{Au^{I}}$(mm/s)	$\mathrm{Au^{III}}$(mm/s)
AuCl(DBS)	1.01	
$AuCl_2$(DBS)	1.09	1.40
$AuCl_3$(DBS)		1.59
$[Bu_4N][AuCl_2]$	0.31	
$Cs_2[\mathrm{Au^{I}}Cl_2][\mathrm{Au^{III}}Cl_4]$	-1.07	0.34
$[Bu_4N][AuCl_4]$		1.02

Table 1 Isomer shifts of Au in $AuCl_X$(DBS)(X=1, 2, 3), $Cs_2[AuCl_2][AuCl_4]$[9],[Bu4N]$[AuCl_2]$[10],and[Bu4N]$[AuCl_4]$[11], Relative to gold in platinum.

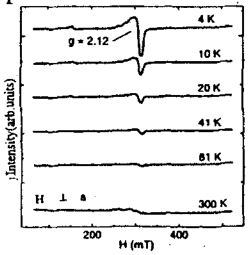

Figure 4 Temperature dependence of the ESR spectra of $AuCl_2$(DBS)

Figure 5 shows the X-ray powder patterns of AuX_2(DBS) (X=Cl, Br). As shown in Fig.5, the X-ray powder patterns of AuX_2(DBS) (X=Cl, Br) shows these two complexes to be isomorphous. Now we are performing the single crystal X-ray structural analysis of $AuBr_2(DBS)$.

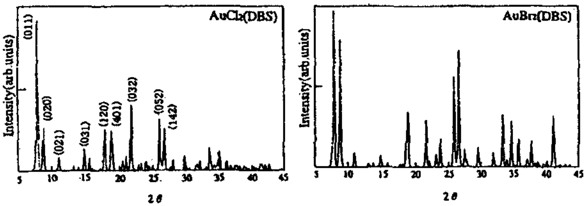

Figure 5 X-ray powder patterns of $AuX_2(DBS)$ (X=Cl,Br)

Acknowledgments

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