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Evidences for Bromo-Bridged One-Dimensional Chain Structure of the Mixed-Valence Gold Complexes with the Empirical Formulas, [$AuBr_2$(DBS)] and [AuBrCl(DBS)] (DBS = dibenzyl sulfide)

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The bromo-bridged one-dimensional chain structure of [$AuBr_2$(DBS)] is revealed by X-ray analysis. The bromo-bridged skeleton of the one-dimensional chain of [AuBrCl(DBS)] is identified by comparing its unit cell parameters, visible absorption spectrum on nujol mull, and Br K near-edge X-ray absorption spectra with those of [$AuBr_2$(DBS)].

Halogen-bridged one-dimensional (1-d) mixed-valence complexes have been attracted much attention from the viewpoint of low-dimensional compounds.[1)] The gold complexes with an empirical formula, [AuX_2(DBS)] (X = halogen), are known to be a limited examples of the halogen-bridged 1-d Au(I)-Au(III) mixed-valence complexes.[2,3)] Though detailed structural information of these DBS-gold complexes have been required to study correlations between those 1-d chain structures and physical properties, only the crystal structure of [$AuCl_2$(DBS)] has so far been determined.[4)] Thus structural studies of the DBS-gold complexes are much to be desired. In our previous study on optical properties of the DBS-gold complexes, the 1-d chains of [$AuBr_2$(DBS)] (**1**) and [AuBrCl(DBS)] (**2**) were presumed to be a bromo-bridged type similar to the chloro-bridged 1-d chain of [$AuCl_2$(DBS)], based on the analogies among those crystal shapes, dichroic behaviors of light absorption, etc.[5)] In this study, we have analyzed the crystal structure of **1** by X-ray diffraction method in order to reveal the bromo-bridged feature and the structural parameters of its 1-d chain. The crystals of **2** were too small to analyze its structure by the X-ray method. The structural information of **2** have been acquired by comparing its unit cell parameters, visible absorption spectra, and X-ray absorption spectra with those of **1**.

1 was prepared by the literature method.[3)] Deep brown dichroic needle crystals were obtained by recrystallization from a $CHCl_3$–$BrCH_2CH_2Br$(5 vol%)

solution. Brown dichroic needle crystals of **2** were obtained by slow evaporation of solvent of the mixed solution of a $CHCl_3$ solution (15 ml) of $[Au^{I}Cl(DBS)]$[6] (1 g) and a CCl_4 solution (5 ml) of Br_2 (180 mg) at 0 °C.[7]

The crystals of **1**, which looked just like good single crystals, were severely twinned crystals, and were cleaved along the needle direction. The crystal used in this X-ray study was chosen among the cleaved crystals.[8] Crystal data of **1**: $C_{14}H_{14}SBr_2Au$; FW=571.1; monoclinic; $P2_1/n$; a=5.720(2), b=13.544(1), c=20.116(4) Å; β=97.63(2)°, V=1544.6(9) $Å^3$; Z=4; D_m, D_c=2.5, 2.45 gcm^{-3}; crystal size=0.05×0.08×0.20 mm^3. The bromo-bridged 1-d chain structure and the crystal structure of **1** are shown in Fig. 1 (a) and (b), respectively. The 1-d direction is parallel to the a-axis, and to the needle direction of the crystal. The alternate arrangement of the two component complexes, $[Au^{I}Br(DBS)]$ and $[Au^{III}Br_3(DBS)]$, can not be identified due to the positional disorder of the bridging bromide (Br(1) and Br(2) in Fig. 1 (a), they slightly deviate from the Au–Au′ vector). Neither diffuse scattering nor Bragg reflection indicating a superstructure along the a-axis was discerned on X-ray oscillation photographs. It should be noted that the structural features of this bromo-bridged chain described above are essentially the same as those of the chloro-bridged chain of $[AuCl_2(DBS)]$.[4] The average distance (2.41 Å) of Au–Br(1) and Au–Br(2) is almost equivalent to the lengths of the three Au–Br coordination bonds (2.41–2.43 Å) of the mononuclear complex, $[Au^{III}Br_3(DBS)]$ (**3**).[9] Hence, the significant interatomic distances in the 1-d chain skeleton, i.e., Au^{III}—Br and Au^{I}···Br, can be estimated to be 2.41 and 3.34 Å, respectively, where the latter is the average value of Au···Br(1)″ (3.30(1) Å) and Au···Br(2)′ (3.37(1) Å). As seen in Fig. 1 (b), the pairing of the two 1-d chains (interchain distance ≃ 3.30 Å) is observed. The constituent complex entities in each chain stack into a face to face like fashion. Similar chain pairing is observed in the $[AuCl_2(DBS)]$ crystal.[4]

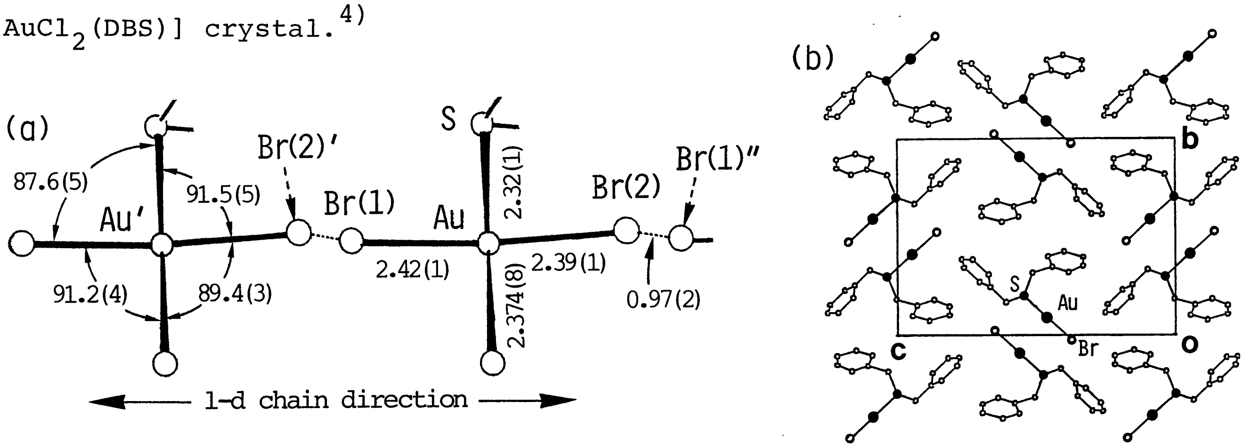

Fig. 1. (a) View of a fraction of the 1-d chain structure of **1**. The bond distances(Å) and angles(°) are entered in the right and the left fragments, respectively. Occupancy factors of Br(1) and Br(2) are assumed to be 0.5. Benzyl groups are omitted for clarity. (b) Crystal structure viewed along a-axis. Br(1) and Br(2) are omitted for clarity.

The unit cell parameters of the three small crystals of **2** were determined. The approximate unit cell dimensions of these crystals are: a=5.7, b=13.5, c=20.1 Å, and β=98°. These values and the values of *FW* (526.7) and D_m (2.3 $\mathrm{gcm^{-3}}$) lead to $Z\simeq4$. The unit cell parameters of **2** are similar to those of **1**. The crystal structure of **2** may be analogous to that of **1**.

Figure 2 shows the visible absorption spectra of **1** and **2** on nujol mull, and that of **3** in $CHCl_3$. In the solid spectra, two absorption bands are distinctly observed around 19×10^3 $\mathrm{cm^{-1}}$ (abs. max.: **1** 18.4×10^3 $\mathrm{cm^{-1}}$, **2** 19.2×10^3 $\mathrm{cm^{-1}}$) and 22×10^3 $\mathrm{cm^{-1}}$ (shoulder). The lower energy band is absent in solution, where the solution spectra of **1** and **2** in $CHCl_3$ are the same as and similar to that of **3**, respectively. By these observations, **1** and **2** are ascertained to be a lattice compound of Au(I) and Au(III) component complexes, and the lower energy band can be attributed to a strong charge transfer (CT) interaction from Au^+ to Au^{3+} through the 1-d chain skeleton. From the dichroism of the crystals of **1** and **2** for visible light, we have already confirmed the fact that this CT is highly polarized along the 1-d chain direction.$^{5)}$ The shoulder in solid spectra is assignable to the ligand to metal ($Br^-\rightarrow Au^{3+}$) CT band,$^{10)}$ since a very broad band is observed around 23×10^3 $\mathrm{cm^{-1}}$ in the solid spectra of **3**.

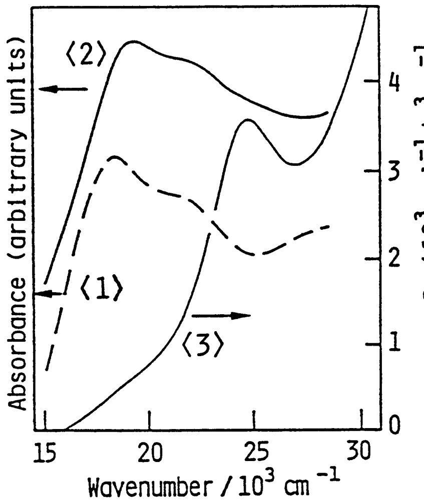

Fig. 2. Absorption spectra of the powdered samples of **1** and **2** on nujol mull, and that of **3** in $CHCl_3$.

The polarized Br K near-edge X-ray absorption spectra of the needle crystals of **1** and **2** are given in Fig. 3.$^{11)}$ Each crystal shows a similar dichroism, which is consistent with that for visible light. When the polarization direction of an incident X-ray is parallel to the needle direction of the crystal, a sharp peak so-called white line (WL)$^{12)}$ is observed at the absorption edge in each spectrum (peak energy: **1** 13.477 keV, **2** 13.476 keV). This WL is attributed to an electronic transition from 1s orbital to a partially unoccupied molecular orbital generated from 4p orbital of a covalently bound Br atom (briefly termed "the 4p state of Br"), and is expected to disappear in the case of Br^- alone with a fulfilled subshell, $4p^6$.$^{13)}$ The intensity of the WL is directly related to the electron density of the 4p state of Br, and reflects magnitude of a CT through a chemical

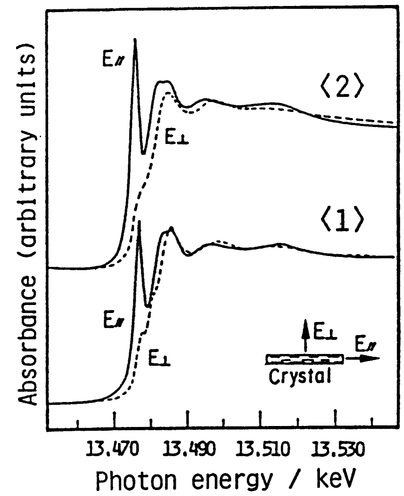

Fig. 3. Polarized Br K near-edge X-ray absorption spectra of the needle crystals of **1** and **2**.

bond.[13)] The 4*p* state of the bridging bromide of **1** is expected to be partially unoccupied, because this ligand is the pathway of the strong $Au^{+} \rightarrow Au^{3+}$ CT through the 1-d chain. It can be deduced from these interpretations that the intense WL in the spectra of **1** and **2** arises from the bridging bromide in those 1-d chains. A very weak peak of the WL is observed at 13.477 keV in the spectrum of **1** when the polarization direction of the X-ray is perpendicular to the needle direction. This may be due to less covalent (more ionic) nature of the bromide trans to DBS than that of the bridging bromide. In the case of **2**, no peak corresponding to the WL is observed in its spectrum.

The above spectroscopic results suggest that the bridging ligand in the 1-d chain of **2** is substantially bromide. The chloride in **2** seems to be the trans ligand of DBS.

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7) Elemental analysis of **2** : Found: C, 31.53; H, 2.61; S, 6.02; Cl 6.59%. Calcd for $C_{14}H_{14}SClBrAu$: C, 31.93; H, 2.68; S, 6.09; Cl, 6.73%. This complex was not recrystallized, because the compositions of elements of the recrystallized crystals were non-stoichiometric.
8) This crystal was selected under examination of qualities of many cleaved crystals by measurements of peak profiles (on diffractometer) and shapes of spots (on photographs) of X-ray reflections. This examination showed a slight twinning on this crystal (twin axis is *a*). In this analysis, the distribution of twin individuals has not been considered, and the intensity measurement made for reflections from the largest (predominant) individual. The structure has been able to analyze by employing the monoclinic crystal system with the space group $P2_1/n$, and has been refined to R=0.124 (thermal parameters: anisotropic for Au, Br, and S; isotropic for C) using 1474 unique reflections with $I > 3\sigma(I)$ (measured on an Enraf-Nonius CAD4 diffractometer with Mo K_α radiation; corrected for the Lorentz-polarization effect, absorption, and extinction).
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11) The X-ray absorption spectra were measured at room temperature under inert gas atmosphere, using a synchrotron radiation (polarized X-ray beam, 2.5 GeV, 60–200 mA, resolution of energy < 1 eV at 9 GeV, monochromated by a Si(311) channel-cut crystal) on the EXAFS station at the Beam Line 10B in the Photon Factory of National Laboratory for High Energy Physics (KEK). We briefly described the polarized Br K near-edge spectra of **2** in the *KEK Photon Factory Activity Report*, **4**, 176(1986).
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