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Crystal Structure of Chloro-Bridged One-Dimensional Mixed-Valence Gold Complex with Empirical Formula $[AuCl_2\{S(C_7H_7)_2\}]$

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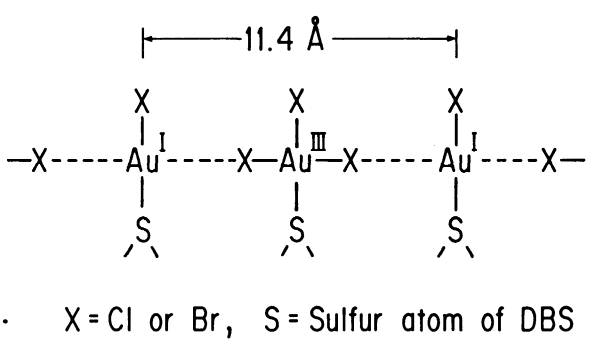
The crystal structure of the title compound is determined by X-ray analysis. The chloro-bridged one-dimensional structure is identified. The bridging chlorine atom has a positional disorder in the crystal. The two one-dimensional chains stack in a face-to-face form with an interchain distance of 3.32 Å.

With interest in halogen-bridged one-dimensional(1-d) mixed-valence complexes as low-dimensional compounds, much attention has been paid to their crystal structures and physical properties based on the charge transfer interaction in the one-dimensional chain. Recently, halogen-bridged mixed-valence platinum complexes so-called 'Wolffram's red salt analogues' and their palladium, nickel and mixed-metal families have been studied as typical compounds of the $5d^6$-$5d^8$ mixed-valence systems.1) In contrast to the extensive studies on a number of the 1-d Pt complexes, a few 1-d Au(I)-Au(III) mixed-valence complexes have been reported so far(empirical formula: $[AuX_2(DBS)]$(X=halogen, DBS=dibenzyl sulfide).2,3) Their structures and physical properties are different from those of the 1-d Pt complexes and it is important to investigate the characteristics of these 1-d $5d^8$-$5d^{10}$ mixed-valence systems. However, their structures have not yet been determined. Only a presumed 1-d structure illustrated below was suggested by Brain et al. in 1952 on the bases of a preliminary X-ray study,3) and only a few studies of physical properties of the gold complexes from the viewpoint of low-dimensional compounds have been reported.4) Therefore, we have started to study the structures and physical properties of the DBS-gold mixed-valence complexes in order to reveal the detailed nature of these $5d^8$-$5d^{10}$ 1-d systems.



Presumed 1-d structure of $[AuX_2(DBS)]$.3)

We have in this study determined the crystal structure of $[AuCl_2(DBS)]$, and reported some features and structural parameters of the 1-d chain.

Crude crystals of $[AuCl_2(DBS)]$ was prepared by the literature method.2) The single crystal suitable for X-ray work was obtained by recrystallization from a chloroform solution at ca. 5 °C for 4 weeks. Needle-shaped orange crystal shows a dichroism under observation by a polarizer. Found: C, 35.02; H, 2.91; Cl, 14.0%.

Crystal data: Formula=$C_{14}H_{14}SCl_2Au$, FW=482.2, monoclinic system with the space group $P2_1/c$, a=5.689(1), b=19.926(4), c=13.432(2) Å, β=93.30(1)°, V=1520.1 $Å^3$, Z=4, Dm, Dc=2.2, 2.11 gcm^{-3}, μ(Mo Kα)=101.3 cm^{-1}. A doubling of the lattice constant of the a-axis was proposed by Brain et al. because of the faint diffuse spots and lines observed in the X-ray oscillation photograph indicating a superstructure along the a-axis.3) In this study, no such diffuseness was observed in the oscillation photographs along the three crystal axes.5) The determination of the crystal structure was based on the independent 2533 reflections(with $I>3\sigma(I)$; corrected for Lorentz-polarization effect, decay and absorption) collected on a Enraf-Nonius four-circle diffractometer CAD4(graphite monochromated Mo Kα radiation) by the ω-2θ scan technique up to 2θ=55° at 295 K. The final R and R_w $(w=1/\sigma|Fo|^2)$ values are 0.031 and 0.035, respectively.

A fraction of the 1-d chain structure is shown in Fig. 1. Selected interatomic distances and angles are listed in Table 1. The skeleton of the 1-d infinite chain is a chloro-bridged type, consisting of Au and Cl atoms. The 1-d direction of the chain is parallel to the a-axis of the crystal. According to our preliminary polarized X-ray absorption work, the 1-d direction is also parallel to the needle direction of the single crystal of $[AuCl_2(DBS)]$.6) In the 1-d chain, a positional disorder of the bridging chlorine atom(Cl(1) and Cl(2) in Fig. 1) has been observed. This seems to arise from the thermal disorder at the temperature of the present X-ray experiments. Since the peak heights corresponding to Cl(1) and Cl(2) in Fourier synthesis were almost the same, their occupancy factors have been assumed to be 0.5 in the structure refinements.7) Cl(1) and Cl(2) slightly deviates from the Au-Au' vector in the 1-d direction.

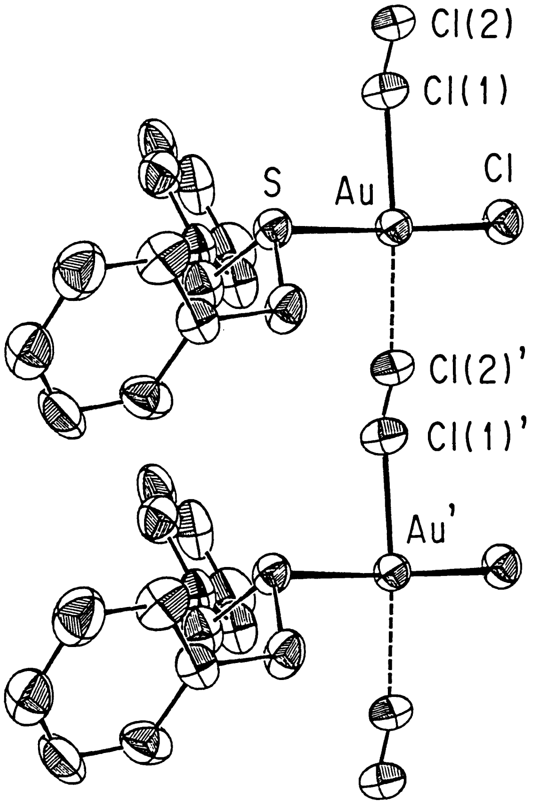


Fig. 1. Perspective view of the 1-d chain structure along the a-axis of $[AuCl_2(DBS)]$.

Table 1. Selected bond distances and angles of the first coordination sphere and the linear chain of $[AuCl_2(DBS)]$

Distances/Å

Au- Cl	2.280(2)	Au- S	2.291(2)
Au-Cl(1)	2.257(3)	Au-Cl(2)	3.374(3)
Au-Cl(1)'	3.440(3)	Au-Cl(2)'	2.321(3)
Cl(1)-Cl(2)	1.133(5)		

Angles/°

Cl-Au-S	177.91(6)
Cl(1)-Au-Cl(2)	4.1(2)
Cl(1)-Au-Cl(2)	175.1(1)
Au-Cl(1)-Cl(2)	168.0(3)
Au-Cl(2)'-Cl(1)'	168.8(3)

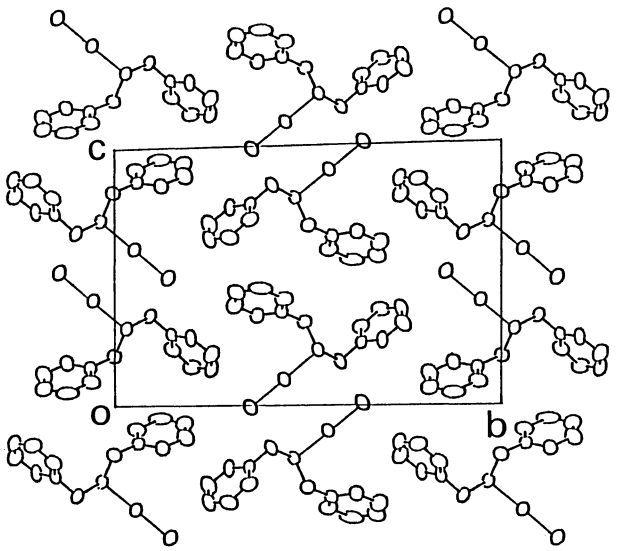


Fig. 2. Crystal structure projected along a-axis. Cl(1) and Cl(2) are omitted for clarity.

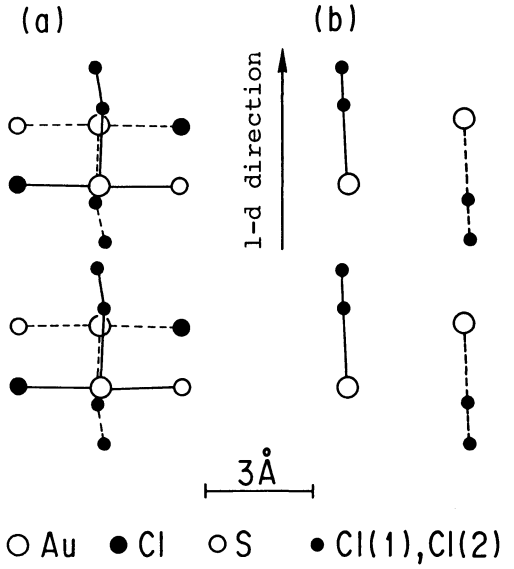


Fig. 3. Overlapping mode between the two adjacent 1-d chains. (b) is rotated 90° from (a).

Owing to the disorder of the bridging chlorine, the alternate arrangement of the Au(I) and Au(III) components depicted in the presumed 1-d structure and significant structural parameters of the 1-d chain have been unable to determine in this X-ray analysis. It is interesting to note here that the average distance of Au-Cl(1) and Au-Cl(2)', 2.29 Å, is nearly equal to the corresponding Au-Cl bond distances in the mononuclear DBS-Au(III) complex, $[AuCl_3(DBS)]$(average 2.272 Å).[8)] This fact suggests that the average distance can be regarded as the Au-Cl(bridging) bond length of the Au(III) component. The Au(I)···Cl(bridging) distance is also estimated as the average of Au-Cl(2) and Au-Cl(1)' distances, 3.41 Å. By employing the above estimated distances, the Au(III)-Cl/Au(I)···Cl ratio of the $5d^8$-$5d^{10}$ 1-d chain is evaluated to be 0.67. Other coordination bond lengths, Au-Cl and Au-S, are within the range between those of the mononuclear Au(I) complex, [AuCl(DBS)],[9)] and the Au(III) complex, $[AuCl_3(DBS)]$.[8)]

Figure 2 shows the crystal structure of $[AuCl_2(DBS)]$. A prominent feature of the crystal structure is the pairing of two 1-d chains. The interchain distance, 3.32 Å, is shorter than the estimated Au(I)···Cl(bridging) distance(3.41 Å). As seen in Fig. 3, the constituent complex entities in each 1-d chain stack in a face-to-face like structure. The selected intermolecular distances between close-neighbouring molecules in the chain pair are: Au-Au" 3.8012(3). Au-Cl(1)" 3.421(4), Au-Cl(2)" 3.745(3), Cl-S" 3.818(3) and Cl(2)-Cl(2)" 3.622(5) Å(symmetry code of " marked atoms: 1-x,-y,1-z). Such an interchain stacking have not been observed in the crystal structures of a number of halogen-bridged mixed-valence Pt complexes and even in these analogues.

The 1-d chain of $[AuCl_2(DBS)]$ is electrically neutral since both the Au(I) and Au(III) components are neutral molecules. Because of the electroneutrality and the essential square-planar coordination geometry of the component molecules, the stacking between two 1-d chains seems to be attributed to an intermolecular interaction between the adjacent Au(I) and Au(III) components. We note that a charge transfer absorption considered as an intermolecular interaction in the 1-d chain pair has been observed by optical measurements.10)

The optical studies will be reported elsewhere, and characterization and structural studies of the series of DBS-gold complexes are now in progress.

We wish to express our thanks to Dr. Takafumi Yao and Dr. Takehiko Ishiguro for their helpful advices and continuous interests.

References

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5) The apparatus of oscillation photograph used in this work is an AXIAL Photo of the optional device of CAD4.

6) K. Takahashi and H. Tanino, Photon Factory Activity Report, 4, 176(1987).

7) When the occupancy factors of Cl(1) and Cl(2) were refined by the full-matrix Least-squares refinements, these values little deviated from 0.50.

8) K. Takahashi, to be submitted. A part of the crystal, experimental, and structural data are described below.
Crystal data are: $C_{14}H_{14}SCl_3Au$, orthorhombic, space group Pnma, a=13.330(2), b=16.132(3), c=7.6947(9) Å, V=1654.7 $Å^3$, and Z=4. 1314 independent reflections have been refined to R=0.032. The Au, S, and three Cl atoms are located at the (x, 1/4, z) positions. The coordination geometry of the molecule is a four-coordinated square planar. The bond distances of Au-S, Au-Cl(trans to S), and two Au-Cl are 2.310(3), 2.287(4), 2.272(3), and 2.272(2) Å, respectively.

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