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Crystal and Electronic Structures of (BEDT-TTF)$AuCl_2AuCl_4$

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Electrochemical crystallization of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) in the presence of $AuCl_4^-$ has yielded an organic conductor with the composition of (BEDT-TTF)$AuCl_2AuCl_4$. X-ray analysis shows that the $AuCl_2^-$ anions are incorporated in the two-dimensional network of BEDT-TTF, and these networks are separated by the $AuCl_4^-$ anions.

The counter anions of organic superconductors reported so far have extended to octahedral (PF_6^-, AsF_6^-, SbF_6^-, and TaF_6^-), tetrahedral (ClO_4^- and ReO_4^-), and linear anions (I_3^-, IBr_2^-, and AuI_2^-).[1] Since the discovery of superconductivity in β-(BEDT-TTF)$_2AuI_2$, several AuX_2^- (X=halogen) salts of BEDT-TTF have been prepared (Ref. 2 and references therein). In contrast to these linear AuX_2^- anions, AuX_4^- has square planar structure,[3] but no organic conductor including such a square planar anion has been investigated. Attempting to prepare an $AuCl_4^-$ salt of BEDT-TTF, we have obtained an organic conductor with the composition of (BEDT-TTF)$AuCl_2AuCl_4$. Concerning this salt, the present paper provides the results of the X-ray structure analysis, the measurement of the electrical resistivity, and discussion of the electronic structure.

Crystals in the form of very thin plates were grown by electrochemical crystallization of BEDT-TTF in benzonitrile using tetrabutylammonium tetrachloroaurate(III) as a supporting electrolyte.[4] Found: C, 12.36; H, 0.87; N, 0.05%. Calcd for $C_{10}H_8S_8Au_2Cl_6$: C, 12.12; H, 0.81; N, 0.00%. The structure analysis confirmed their composition to be (BEDT-TTF)$AuCl_2AuCl_4$ (vide infra). It is not surprising that $AuCl_2^-$ is produced in the reaction cell, because $AuCl_4^-$ is reduced so easily that the redox potential of the reaction,

$$AuCl_4^- + 2\,e^- \rightarrow AuCl_2^- + 2\,Cl^- \qquad (1)$$

is as high as +0.68 V vs. SCE.[5] This potential is comparable with the oxidation potential of BEDT-TTF, +0.53 V.[6] In the case of $AuBr_4^-$, a similar reaction occurred, and produced the compound with the composition of (BEDT-TTF)$_2AuBr_2AuBr_4$-(C_6H_5CN).[7] It has been also known that an inorganic salt $Cs_2Au_2Cl_6$ contains both $AuCl_2^-$ and $AuCl_4^-$.[3]

The crystal data are: monoclinic, space group C2/m, a=7.683(2), b=9.375(2), c=16.079(5) Å, β=98.55(2)°, V=1145.3(5) Å^3, and Z=2. Intensity data were collected by θ-2θ scan technique on a Rigaku automated four-circle diffractometer AFC-5

Table 1. Atomic parameters ($\times 10^4$) of (BEDT-TTF)$AuCl_2AuCl_4$

Atom	X	Y	Z	B_{eq}
Au(1)	0	0	0	2.7
Au(2)	5000	0	5000	3.2
Cl(1)	472(6)	0	1436(3)	4.4
Cl(2)	2023(9)	1779(7)	-29(5)	5.0
Cl(3)	3186(6)	0	3750(3)	4.1
S(1)	1204(4)	1521(2)	5913(2)	3.2
S(2)	3370(5)	1884(3)	7550(2)	4.0
C(1)	512(19)	0	5396(8)	2.4
C(2)	2364(12)	736(10)	6804(6)	2.6
C(3)	4519(28)	645(15)	8289(11)	9.4

with graphite monochromatized Mo-Kα radiation ($2\theta<60°$). Lorentz and polarization effects, and absorption corrections were performed. The structure was solved by the Patterson method and refined by the block-diagonal least-squares procedure (R=0.053) by using 1317 independent reflections. The hydrogen atoms were not included in the refinement, and anisotropic thermal parameters were adopted for all other atoms.

The atomic coodinates are listed in Table 1. The crystal structure is shown in Fig. 1. The Au(1), Au(2) atoms and the center of the BEDT-TTF molecule are present on 2/m positions, and Cl(1), Cl(3), and C(1) on mirror planes. The BEDT-TTF molecules and the $AuCl_2^-$ anions are stacked alternately along the a axis. However, the BEDT-TTF molecules form a two-dimensional network parallel to the ab plane (Fig. 2); the arrangement of the BEDT-TTF molecules corresponds to the C-centered lattice. The $AuCl_2^-$ anions are incorporated in this donor network. The angle between the molecular plane of the donor and the direction of the nearest neighbor donor interaction is 36°, and this interaction leads to a considerable orbital (HOMO) overlap of

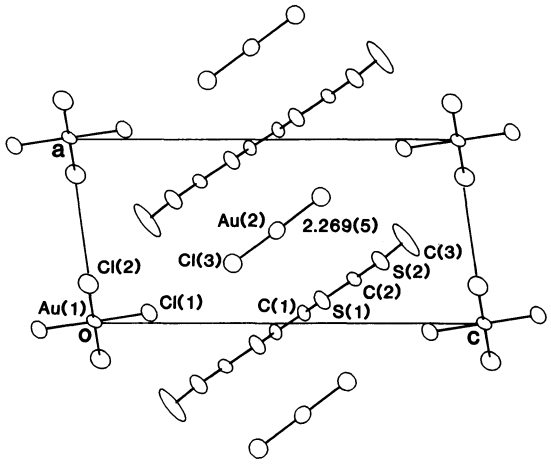

Fig. 1. Crystal structure of (BEDT-TTF)$AuCl_2AuCl_4$, viewed along the b axis.

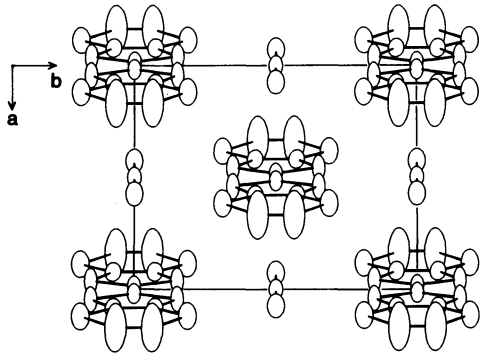

Fig. 2. Structure of the donor-$AuCl_2^-$ sheet.

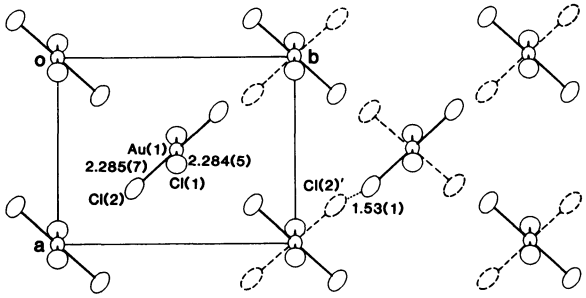

Fig. 3. Structure of the $AuCl_4^-$ sheet. Bond lengths in Å.

Table 2. A comparison of bond lengths (Å)

Bond	Present Salt	(BEDT-TTF)-$ReO_4(THF)_{0.5}$
C(1) - C(1)	1.40(2)	1.38(3)
C(1) - S(1)	1.70(1)	1.72(1)
S(1) - C(2)	1.73(1)	1.73(1)
C(2) - C(2)	1.38(1)	1.37(2)

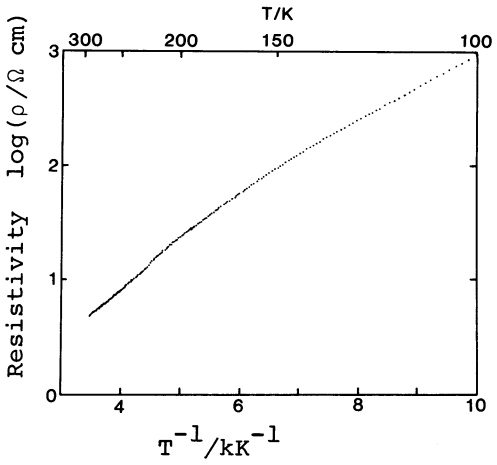

Fig. 4. Electrical resistivity.

the donors (-10.5×10^{-3}, calculated by the method of Ref. 8). Thus, in spite of the interruption by $AuCl_2^-$, the BEDT-TTF molecules form a two-dimensional sheet.

These donor-$AuCl_2^-$ networks are separated from each other by the $AuCl_4^-$ sheets. The structure of the $AuCl_4^-$ sheet is depicted in Fig. 3. If space group C2/m is assumed, there appears an anomalously short Cl···Cl distance, 1.53 Å. Thus, the $AuCl_4^-$ anions are considered to be arranged as depicted with the solid lines in Fig. 3. However, the $AuCl_4^-$ sheets lack the complete order along the c axis; in addition to the very weak hkl (h+k=odd) reflections originating in the ordered Cl(2) atoms (if these reflections are taken into account, the space group would be $P2_1/a$), there are (h,k, l+0.5) (h+k=odd) reflections with comparable intensity (these reflections come from the existence of the sheets illustrated by the dashed lines in Fig. 3). Therefore, the present structure analysis was carried out by assuming the space group C2/m, and by setting the population of Cl(2) at 1/2.

The electrical resistivity is shown in Fig. 4. The resistivity is about 4 Ωcm at room temperature and semiconductive with an activation energy of 0.08 eV. The composition, (BEDT-TTF)$AuCl_2AuCl_4$, indicates that the donor is doubly charged as BEDT-TTF^{2+}. However, this comparatively low resistivity seems to conflict with such a completely ionized (possibly diamagnetic) electronic state. Moreover, the agreement of the bond lengths with (BEDT-TTF)$ReO_4(THF)_{0.5}$ (Table 2),[9] which includes BEDT-TTF^+, designates the presence of BEDT-TTF^+. Possible explanations that avoid this annoying situation are:

(1) Anomalous valence states of Au, or another disorder in the $AuCl_2^-$ or $AuCl_4^-$ sheet. These possibilities are, however, very little plausible, because there is no anomaly in the Au-Cl bond lengths and the thermal factors of the anion atoms.

(2) Inclusion of unobserved protons (present probably around the Cl atoms) as (BEDT-TTF)$HAuCl_2AuCl_4$. This assumption does not disagree with the results of elemental analysis. Though origin of the proton is not obvious, this possibility cannot be excluded.

(3) Overlap of the bottom of the HOMO energy band with the top of the next highest band. Therefore, the band structure becomes semimetallic or like a narrow gap semiconductor, in spite of the complete ionization as BEDT-TTF^{2+}. In this case the comparison of the bond lengths like Table 2 is meaningless. Although the

bandwidth (0.4 eV for HOMO, estimated by the molecular orbital calculation) is likely to be less than the energy level separation between HOMO and the next level (0.8 eV by the same calculation), this possibility cannot be excluded.

In the present stage, we cannot make any unambiguous conclusion. It needs futher work to resolve this problem.

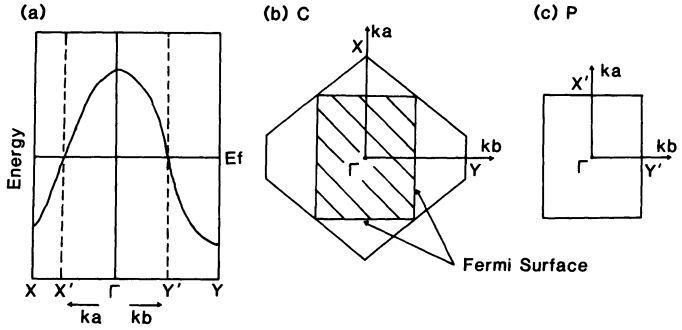

Fig. 5. (a) Energy band structure, (b) the Brillouin zone and the Fermi surface of the C-centered lattice, and (c) the Brillouin zone of the primitive lattice.

In the cases of (1) and (2), the energy band composed of the donor HOMO is half-filled. The tight-binding approximation provides the energy dispersion relation, $E(k)=4t\cos(ka/2)\cos(kb/2)$ (Fig. 5(a)). Since there is no second nearest interaction due to the interruption by $AuCl_2^-$ (Fig. 2), the Fermi surface is rectangular as shown in Fig. 5(b). However, if the primitive unit cell is chosen by considering the order of the $AuCl_4^-$ sheet, the zone boundary exactly corresponds with the Fermi surface (Fig. 5(c)). In other words, if only the uniform two-dimensional network of BEDT-TTF is considered, the band structure is metallic, because the Wigner-Seitz cell (of the C-centered lattice) contains one donor molecule, and the energy band is half-filled. However, the periodic potential of the $AuCl_4^-$ sheet opens a small gap at the Fermi surface, and makes the compound semiconductive. This may be the reason that the present compound exhibits so high room-temperature conductivity as the distorted 2:1 salts, such as δ-$(BEDT\text{-}TTF)_2AuBr_2$.[2)]

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