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The θ-Type Cation Radical Salts of BMDT-TTF, Bis(methylenedithio)tetrathiafulvalene

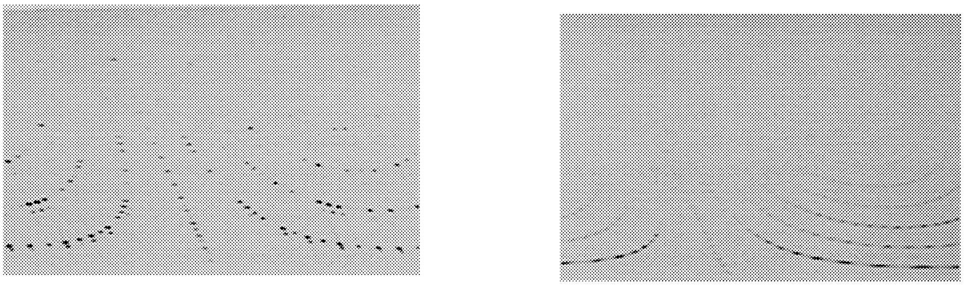
Reizo KATO, Hayao KOBAYASHI, and Akiko KOBAYASHI[†]
Department of Chemistry, Faculty of Science, Toho University,
Funabashi, Chiba 274
†Department of Chemistry, Faculty of Science, The University of
Tokyo, Hongo, Bunkyo-ku, Tokyo 113

The molecular arrangement of BMDT-TTF in crystals of (BMDT-TTF)-X system (X=AuI_2^-, $AuBr_2^-$, and AsF_6^-) is quite similar to that in the organic superconductor θ-$(BEDT\text{-}TTF)_2I_3$. Their electronic properties are, however, different from those of θ-$(BEDT\text{-}TTF)_2I_3$.

The organic donor BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) has been characterized by its ability to form two-dimensional electronic structure. Recently, we have obtained a new ambient-pressure superconductor θ-$(BEDT\text{-}TTF)_2I_3$ which has exhibited two-dimensional crystal and electronic structures.[1)] In this paper, we will report that the θ-type crystal structure is also observed in cation radical salts ($AuBr_2$, AuI_2, and AsF_6 salts) based on BMDT-TTF (bis(methylenedithio)tetrathiafulvalene; abbreviated to MT) but their electronic properties are quite different from those of θ-$(BEDT\text{-}TTF)_2I_3$.

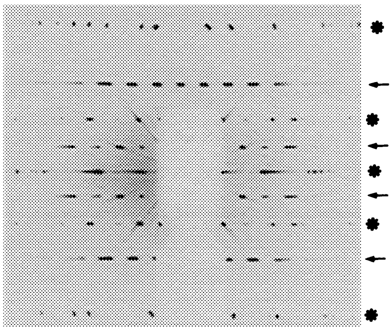
Single crystals of all these compounds were obtained as dark brown thin plates by the galvanostatic electrochemical oxidation of solutions containing MT and corresponding anion.

The crystal of the $AuBr_2$ salt is almost isostructural with θ-$(BEDT\text{-}TTF)_2I_3$.[1)] As is the case of the θ-salt, the X-ray diffraction patterns of the $AuBr_2$ salt contain two quite different types of reflections, normal type-I and monotonous type-II reflections (Figs. 1 and 2). The type-II reflections arise from $AuBr_2$ sublattice and somewhat diffusive, indicating disordered anion arrangement. The crystal data based on the type-I reflections are: $(C_8H_4S_8)_2AuBr_2$, orthorhombic, Pnma, a=10.406(2), b=31.453(9), c=4.163(1) Å, V=1362.5 $Å^3$, Z=2. An average structure (Fig. 3) was solved and refined using 978 independent type-I reflections (Mo Kα, $2\theta \leq 60°$, $|F_o| > 3\sigma(|F_o|)$). The final R value was 0.104. The MT units repeat along the crystallographic c axis. Since the normal to the MT molecular plane is largely tilted (30°) with respect to the c axis, the overlap of the molecular planes is small (Fig. 4). No short S•••S distance (<3.7 Å; the van der Waals radii sum) is observed along this direction. On the other hand, the "herringbone" arrangement of the inclined MT molecules with dihedral angle of 61° forms the two-dimensional S•••S network parallel to the ac plane (Fig. 5). This

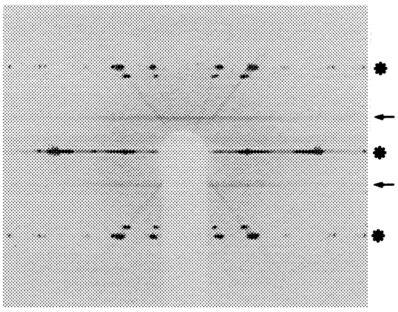


(a) (b)

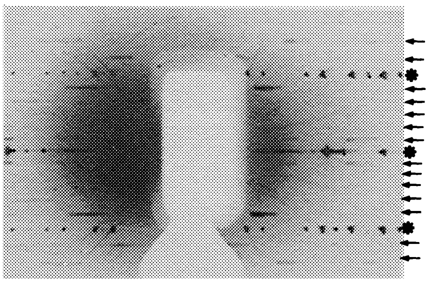
Fig. 1. Weissenberg photographs of $(MT)_2AuBr_2$. (a) Type-I reflections. (b) Type-II reflections.



(a) $AuBr_2$ salt



(b) AuI_2 salt



(c) AsF_6 salt

Fig. 2. Type-I(✱) and II(←) reflections observed in oscillation photographs.

Table 1. Fractional atomic coordinates (× 10^4) with their estimated standard deviations for $(MT)_2AuBr_2$

Atom	x	y	z
S(1)	-740(5)	609(2)	3289(18)
S(2)	1595(5)	374(2)	6855(18)
S(3)	159(6)	1529(2)	2825(19)
S(4)	2551(5)	1289(2)	6443(17)
C(1)	183(20)	192(7)	4994(67)
C(2)	366(20)	1006(5)	4038(60)
C(3)	1411(20)	905(6)	5739(64)
C(4)	1604(26)	1733(9)	4792(93)
Au	4117(3)	2500	1765(10)
Br	4124(7)	2500	6756(23)

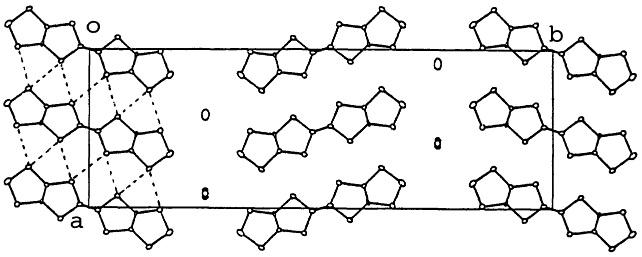


Fig. 3. Crystal structure of $(MT)_2AuBr_2$. Short S•••S contacts (<3.7 Å) are indicated by dotted lines.

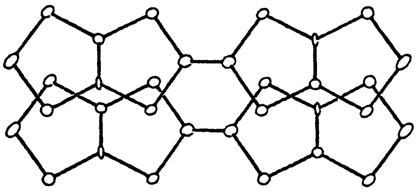


Fig. 4. Mode of overlapping in $(MT)_2AuBr_2$.

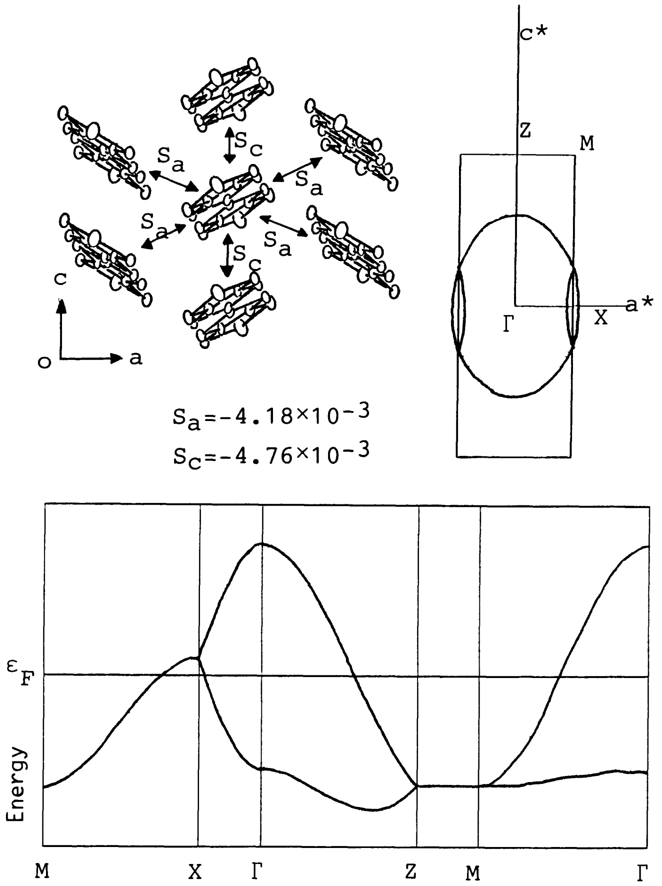


Fig. 5. Overlap integrals of the HOMO, band structure, and Fermi surface of $(MT)_2AuBr_2$.

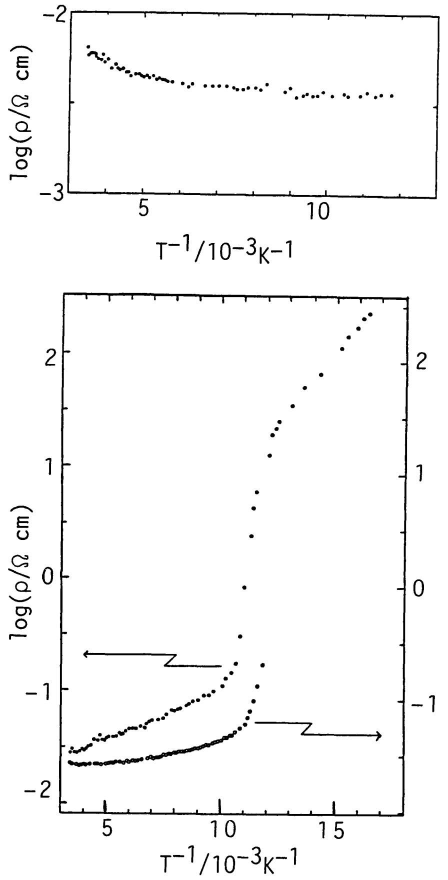


Fig. 6. Electrical resistivity of $(MT)_2AuBr_2$ (3 samples).

value of the dihedral angle (61°) is smaller than that in the θ salt (80°), or rather is very close to those in $(MT)_3ClO_4$(1,2-dichloroethane) (57-58°).[2] This structure, in fact, is closely related to that of the ClO_4 salt. The most important distinction, however, is that in this $AuBr_2$ salt each donor molecule is crystallographically equivalent and there is not the "charge separation phenomenon" observed in the ClO_4 and PF_6 salts.[3]

The calculation of the intermolecular overlap integrals of the HOMO (highest occupied molecular orbital) indicates isotropic intermolecular interactions (Fig. 5).[4] Using the approximation that the transfer integral is proportional to the overlap integral, we have carried out tight-binding band calculation (Fig. 5). The band structure obtained is quite similar to that of the θ salt.[1] Electrical resistivity of this salt, however, shows very different behavior. The temperature dependence of the resistivity, which is somewhat affected by the quality of a crystal, is very small down to ca. 95 K (Fig. 6). Below ca. 95 K, this compound turns a semiconductor. Considering the strong two-dimensional nature observed in the electronic structure, this transition would not be explained by the simple Peierls-type instability.

X-Ray diffraction patterns of the AuI_2 salt also contain the type-II reflections which are more diffusive than those of the $AuBr_2$ salt. The intensity distribution of the type-I reflections is almost identical with that of the $AuBr_2$ salt, but the periodicity of the type-II reflections is quite different (Fig. 2). These results suggest that the molecular arrangement of MT in this AuI_2 salt is the θ-type one and the difference in the reflection patterns arises from the highly disordered anion sites. Electrical resistivity measurements show that the AuI_2 salt exhibits metal-semiconductor transition at ca. 210 K ($\sigma_{R.T.}$= ca. 10^2 S cm^{-1}).

Crystal data of the AsF_6 salt are: monoclinic, C2/c, a=34.661(8), b=4.072(2), c=10.894(4) Å, β=95.94(3)°, V=1529.3 $Å^3$. X-ray diffraction patterns also contain diffusive type-II reflections which arise from highly disordered anion sites (Fig. 2). Although the symmetry of the system is reduced to monoclinic, an average structure solved using 873 independent type-I reflections ($2\theta \leq 60°$, $|F_o| > 3\sigma(|F_o|)$) exhibits the θ-type "herringbone" network of MT molecules. The dihedral angle between the inclined MT molecular planes is 55°. Each MT molecule is crystallographically equivalent. The position and orientation of AsF_6 anions are highly disordered, and refinement of the site occupacy factor of As atom suggests the formulation of $(MT)_2AsF_6$. The final R value was 0.12. The calculated band structure and Fermi surface for the two-dimensional network of $MT^{1/2+}$ molecules are very similar to those of the $AuBr_2$ salt. This compound shows resistivity minimum at ca. 300 K ($\sigma_{R.T.}$= ca. 4 S cm^{-1}).

In the MT molecule, the terminal ethylene groups in BEDT-TTF, which prevent close face-to-face contact, are replaced by the methylene groups.$^{2)}$ Thus, the interplanar distance is reduced in the MT salts (3.8→3.6 Å), leading to the change of the dihedral angle between the inclined molecules (80° → ca.60°). In the θ-type crystal structure, the anions are located in the tunnel-like cavities sandwiched between the cation network. The less crowded methylene group brings these cavities capacity to hold counter anions with various size and shape. The distinct feature of θ-$(BEDT\text{-}TTF)_2I_3$ is the ordered anion arrangement.$^{1)}$ On the other hand, the anion sites in all these θ-type MT salts are disordered.

Although these θ-type MT salts have a strong resemblance to θ-$(BEDT\text{-}TTF)_2I_3$, they are semiconductive at low temperature. In order to examine an effect of the disordered anion site and a possibility of the charge separation at the semiconductive state, X-ray crystallographic study at low temperature is in progress.

References

1) H. Kobayashi, R. Kato, A. Kobayashi, Y. Nishio, K. Kajita, and W. Sasaki, Chem. Lett., 1986, 789, 833.
2) R. Kato, H. Kobayashi, A. Kobayashi, and Y. Sasaki, Chem. Lett., 1984, 1693.
3) R. Kato, H. Kobayashi, T. Mori, A. Kobayashi, and Y. Sasaki, Solid State Commun., 55, 387 (1985).
4) The calculations were performed using the program written by Dr. T. Mori. The atomic parameters for the extended Hückel calculations were taken from E. Clementi and C. Roetti, Atomic Data and Nuclear Data Tables, 14, 117 (1974).

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