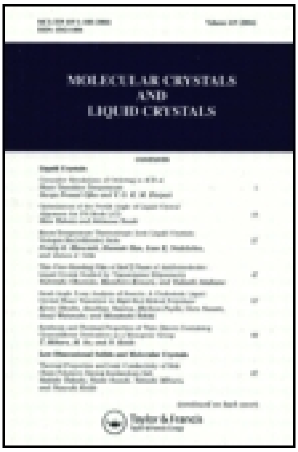


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Physical Properties and Crystal Structures of Charge Transfer Complexes Based on EDOEDT-TTF (EOET)

Takashi Aoki [a], Gunzi Saito [a], Hideki Yamochi [a b] & Mitsuhiko Maesato [a b]

[a] Division of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto, 606-8502, Japan

[b] CREST, Japan Science and Technology Corporation (JST), Japan

To cite this article: Takashi Aoki, Gunzi Saito, Hideki Yamochi & Mitsuhiko Maesato (2002): Physical Properties and Crystal Structures of Charge Transfer Complexes Based on EDOEDT-TTF (EOET), Molecular Crystals and Liquid Crystals, 376:1, 201-206

To link to this article: http://dx.doi.org/10.1080/713738392

Mol. Cryst. Liq. Cryst., Vol. 376, pp. 201-206
Copyright © 2002 Taylor & Francis
1058-725X/02 \$12.00 + .00

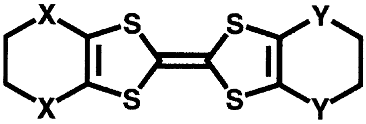
Physical Properties and Crystal Structures of Charge Transfer Complexes Based on EDOEDT-TTF (EOET)

TAKASHI AOKI[a], GUNZI SAITO[a], HIDEKI YAMOCHI[a,b] and
MITSUHIKO MAESATO[a,b]

[a]*Division of Chemistry, Graduate School of Science, Kyoto University,
Sakyo-ku, Kyoto 606-8502, Japan and*
[b]*CREST, Japan Science and Technology Corporation (JST), Japan*

The electrocrystallization of EOET in the presence of $(Bu_4N)AuBr_2$ afforded two kinds of complexes. β''-$(EOET)_2AuBr_2$ shows metallic behavior down to liquid helium temperature, while α'-$(EOET)_2AuBr_2$ is a Mott-Hubbard type semiconductor.

Keywords EDOEDT-TTF; EOET; Mott insulator; Crystal structure; Conductivity; Magnetic property



ET : X=Y=S, BO : X=Y=O
EDOEDT-TTF (EOET) : X=S, Y=O

INTRODUCTION

The organic donors containing TTF skeleton are the basis of large number of conducting and superconducting cation radical salts. Among them, ET has provided many types of two-dimensional (2D) organic superconductors with the variety of crystal structure, while BO has afforded a number of 2D metals having similar packing patterns due to its strong self-assembling ability.

EDOEDT-TTF (EOET) is a hybrid donor of ET and BO synthesized by Kini et al. in 1990 [1]. However, little is known concerning EOET radical salts. We report here the physical and structural properties of two types of radical cation salts with $AuBr_2^-$ and compare their physical properties to those of isostructural ET salts.

EXPERIMENTAL

EOET salts were crystallized by electrochemical oxidation of EOET in 1,2-dichloroehtane with $(Bu_4N)AuBr_2$ as the supporting electrolyte. Usually, both β'' and α' salts were obtained in the same batch. β''-salt is obtained as black block crystals, while α'-salt is black needles.

The resistivity was measured by a standard four-probe (β''-salt) and two-probe (α'-salt) method. Contacts to the single crystals were glued with a gold paste using 15 μm diameter gold wire. The susceptibility was measured using Quantum Design MPMS-XL. The intensity data of the structural analysis were collected on Imaging Plate type diffractometer at room temperature. The structures were solved by a direct method using the SIR92 programs and were refined by the CRYSTAN6.3 and SHELX-93.

RESULTS AND DISCUSSION

β''-salt

β''- $(EOET)_2AuBr_2$ crystallizes in the triclinic space group $P\bar{1}$ with the unit cell parameters of a = 5.425(1), b = 8.983(2), c = 16.127(4) Å, α = 92.36(1), β = 97.92(1), γ = 104.61(1)°, V = 746.5(3) Å^3, Z = 1, R = 0.054.

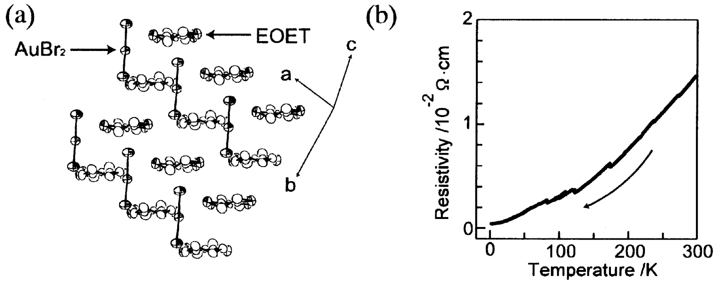


FIGURE 1 Crystal structure (a) and electric resistivity (b) of β''-$(EOET)_2AuBr_2$.

The donor molecules form the weakly dimerized column in the head-to-tail overlap pattern (Figure 1a). This type of packing pattern is similar to that of β''-$(ET)_2AuBr_2$ [2]. The resistivity measurements showed both the room temperature conductivity of $\sigma_{r.t.}$ = 60 Scm^{-1} and the metallic behavior down to 1.6 K, though the resistivity jumps were frequently observed due to the microcracks.

The calculated Fermi surfaces consist of hole pocket around Y and two wavy lines along k_y direction (Figure 2). The shape of Fermi surfaces resembles to those of β''-$(ET)_2AuBr_2$ [2] and $(BO)_2ClO_4$ [3]. The characteristic feature of them including the EOET salt is that all of them are organic metals down to low temperatures, that is consistent with the presence of 2D large Fermi surface.

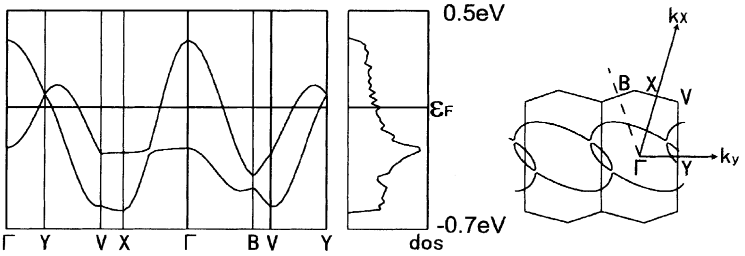


FIGURE 2 Dispersion relation, density of states, and Fermi surface of β''-$(EOET)_2AuBr_2$ calculated by extended Hückel method (left to right).

α'-salt

α'-$(EOET)_2AuBr_2$ crystallizes in the triclinic space group $P\bar{1}$ with the unit cell parameters a = 6.580(3), b = 7.267(3), c = 16.641(5) Å, α = 77.31(3), β = 88.93(2), γ = 84.98(3)°, V = 773.3(6) $Å^3$, Z = 1, R = 0.055.

There are two crystallographically unique EOET molecules, both of which are located on the center of inversion, hence they show the orientational disorder. To solve the crystal structure, we assumed that the sulfur and oxygen atoms occupy the same positions, and ethylene carbon atoms are located at four positions, for all of which the site occupancy factors are assumed to be 0.5. Figure 3a shows the crystal structure of α'-$(EOET)_2AuBr_2$. At Z = 0.5, the donor molecule forms the twisted stack. The donor stacks are uniform, which is different from the dimerized twisted column in α'-$(ET)_2AuBr_2$ [4] and other α'-ET salts [5].

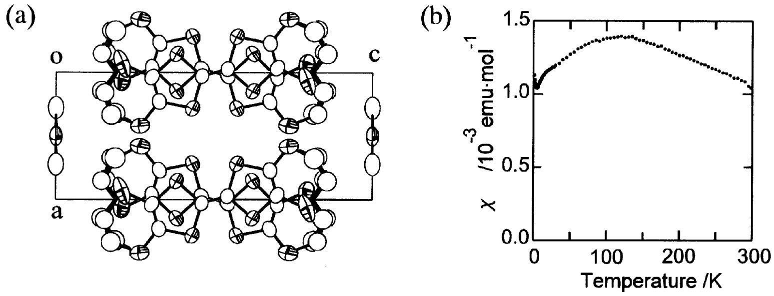


FIGURE 3 Crystal structure viewed along the b-axis (a) and magnetic susceptibility (b) of α'-$(EOET)_2AuBr_2$.

The temperature dependence of the conductivity along the b-axis showed a semiconducting behavior with $\sigma_{r.t.} = 5 \times 10^{-3}$ Scm^{-1} and the activation energy of 0.22 eV (260-310 K).

The temperature dependence of magnetic susceptibility of α'-salt is plotted in Figure 3b. The magnetic susceptibility at room temperature is 1.0×10^{-3} emu•mol^{-1}. The temperature dependence shows a broad maximum around 120K, which is characteristic of short-range antiferromagnetic coupling in low dimensional systems. From that magnetic and transport properties, it is concluded that this salt is not a band insulator, but is a magnetic insulator of the Mott-Hubbard type like α'-ET salts.

CONCLUSION

β''-$(EOET)_2AuBr_2$ and α'-$(EOET)_2AuBr_2$ have similar crystal structures and physical properties to those of β''- $(ET)_2AuBr_2$ and α'-$(ET)_2AuBr_2$, respectively. While the BO molecules do not form this α'-type packing pattern. The behavior of EOET against $AuBr_2^-$ anion is more close to that of ET rather than that of BO.

References

[1] A.M.Kini, T.Mori, U.Geiser, S.M.Budz, and J.M.Williams, J. Chem. Soc. Chem. Commun., 147(1990)

[2] M.A.Beno, M.A.Friestone, P.C.W.Leung, L.M.Sova, H.H.Wang and J.M.Williams, Solid State Commun., **57,** 735-739(1986)

[3] S.Horiuchi, H.Yamochi, G.Saito, K.Sakaguchi, and M.Kusunoki, J. Am. Chem. Soc., **118**, 8604(1996)

[4] D.Chasseau, J.Gaultier, G.Bravic, L.Ducasse, M.Kurmoo and P.Day, Proc. R. Soc. Lond. A, **442**, 207-219(1993)

[5]S.D.Obertelli, R.H.Friend, D.R.Talham, M.Kurmoo and P.Day, J. Phys.: Condens. Matter1, 5671-5680 (1989)