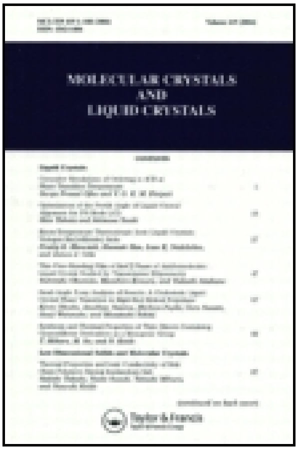

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Unusual Conductive Behavior of $(BEDT\text{-}TTF)_3Cl_2$ Hydrate Salts

Go Ono [a] , Akira Izuoka [a] , Tadashi Sugawara [a] & Yoko Sugawara [b]
[a] Department of Pure and Applied Sciences, Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo, 153, Japan
[b] School of Science, Kitasato University, Kitasato, Sagamihara, Kanagawa, 228, Japan

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UNUSUAL CONDUCTIVE BEHAVIOR OF (BEDT-TTF)$_3$Cl$_2$ HYDRATE SALTS

GO ONO, AKIRA IZUOKA, and TADASHI SUGAWARA*,
Department of Pure and Applied Sciences, Graduate School of Arts and Sciences,
The University of Tokyo, Komaba, Meguro-ku, Tokyo 153 Japan

YOKO SUGAWARA
School of Science, Kitasato University, Kitasato, Sagamihara, Kanagawa 228
Japan

Abstract The ion-radical salt (BEDT-TTF)$_3$Cl$_2$•5H$_2$O has been prepared through electro-crystallization using halocarbons as a solvent in the presence of an aliquot of water. The crystal structure was characterized by a multi-layered structure consists of organic layers of a donor stack and inorganic layers of hydrated chloride ions. When the resistivity was measured, the salt showed a rectifying effect. This effect may be caused by the external field-induced structural transition of chloride ions coupled with the change of a hydration scheme.

INTRODUCTION

If counter ions in organic molecular conductors are connected by dynamic hydrogen bonds, the transport property manifested by conduction columns of the donor stack may be modulated structurally and/or electrostatically. As one of examples of such a system, we have already reported a Ni(dmit)$_2$ complex with a counter ion system which consists of oxonium ions and water molecules.[1] The temperature dependence of conductivity of the salt exhibited a hysteretic loop at around 230 K. This behavior might be ascribed to the change in the hydrogen-bonded network incorporated among the conduction columns.

Recently we have prepared an organic ion-radical salt of a multi-layered structure, consisting of donor layers and layers of hydrated inorganic counter ions. If a certain kind of dynamics of diffusional motions is observed in the counter ion system, it may affect the transport property manifested by the donor layer sandwiched by the former layers. Here we report unusual conductive behaviors of (BEDT-TTF)$_3$Cl$_2$ hydrate salts, and discuss the mechanism of the rectifying effect of this salt.

EXPERIMENTAL

The ion-radical salts of ET with hydrated chloride ions were prepared through an electro-crystallization method using wet halocarbons (CH_2Cl_2 : $CHCl_2CH_2Cl$ = 1:1) as a solvent and n-Bu_4NCl as a supporting electrolyte in a 20 ml H-typed cell equipped with a platinum electrode (5 mm ϕ). The composition of the ET salt was determined by elemental analysis. The electric conductivity was measured by a four or two probe methods. Gold wires (25 μm ϕ) were attached to the sample with gold paste as a contact. The sample was fixed in a chamber in a homemade cryostat and was cooled slowly. The temperature was measured by using an Au-Fe-Chromel thermocouple. Data collection for X-ray structure analysis was performed at room temperature on a Rigaku AFC-7 four-circle diffractometer using monochromatized Cu Kα radiation.

RESULT AND DISCUSSION

The composition of the salt was determined to be ET : Cl : H_2O = 3 : 2 : 5 based on the elemental analysis data. It is different from relevant ET salts containing hydrated chloride ions.[2] The X-ray crystal structure determination was carried out, although the significant disorder in the counter ion layer prohibits the precise analysis at the present stage. The salt consists of ET layers of the α-like structure and layers of hydrated chloride ions (Figure 1).

The conductivity of the salt showed a semiconducting behavior (σ_{rt} = 7.8 Scm^{-1}, Ea = 0.10 eV) when measured along the *b* axis, which is the direction parallel to the multi-layers. The salt, however, showed some unusual transport properties especially

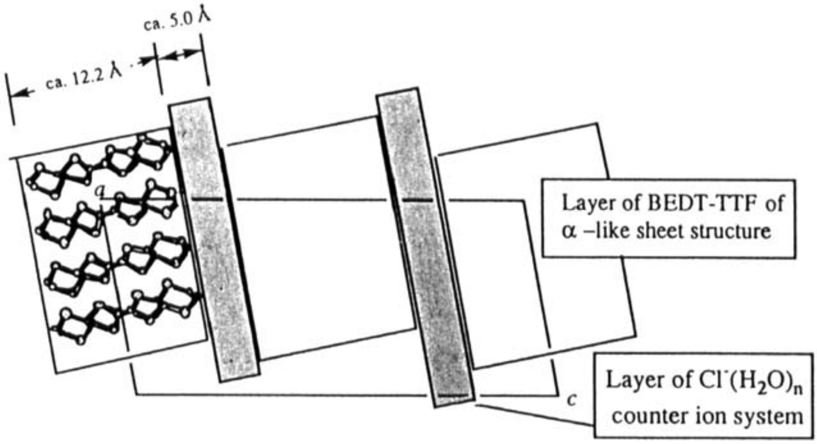

FIGURE 1 Schematic structure of $(BEDT\text{-}TTF)_3Cl_2{\bullet}5H_2O$ (viewed along the *b* axis)

when the resistivity was measured along the *c* axis, which is the transverse direction in reference to the multi-layers. First, when the temperature dependence of the resistivity was measured along the *c* axis, a reproducible hysteretic loop was observed as shown in Figure 2. Namely, a warming trace of the conductivity deviated significantly from the cooling one. The result suggests that some kinds of reversible structural and/or electrostatic changes take place inside the counter ion layer in the specific temperature range and that these changes modulated the transport property on the conducting layers. On the other hand, the hysteresis detected along the *b* axis, was found to be much smaller.

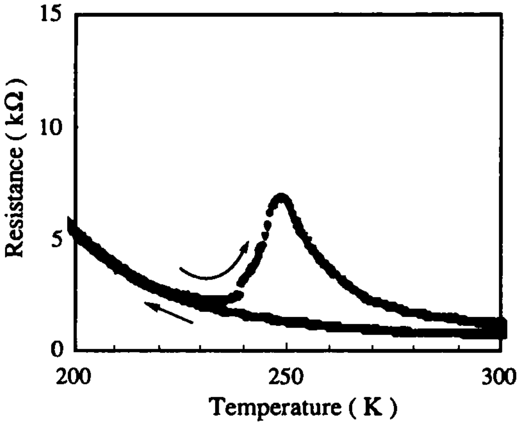

FIGURE 2 Hysteretic loop observed in the temperature dependence of the resistivity of $(BEDTTTF)_3Cl_2 \cdot 5H_2O$ (along the *c* axis)

Second, we happened to find that the resistivity depends on the direction of the direct current as shown in Figure 3 (left). When the direction of the passing current (10 μA ~ 40 μA) was switched from the direction indicated by thick arrows to the dotted one (Figure 3, right), the resistivity increased abruptly. The resistivity turned back to the lower value when the passing direction was reversed. Namely the salt exhibits a rectifying effect. Such a rectifying effect was not observed when the resistivity was measured along the *b* axis. This effect did not appear through a pulse current measurement (10 μA) with a duration time of 5 sec. and an interval of 300 sec..

Third, the high resistivity stage was found to relax to the initial value spontaneously on standing. When the passing current was stopped at the high resistivity state, the resistivity decreased gradually, following an exponential decay curve (Figure 4). The change of resistivity was measured through a pulse current (10 μA, duration time 5 sec., interval 240 sec.), the direction of the current being reversed every two pulses. The temperature dependence of the half life-time of the relaxation process was also measured (52 min. at 300 K, and 97 min. at 276 K).

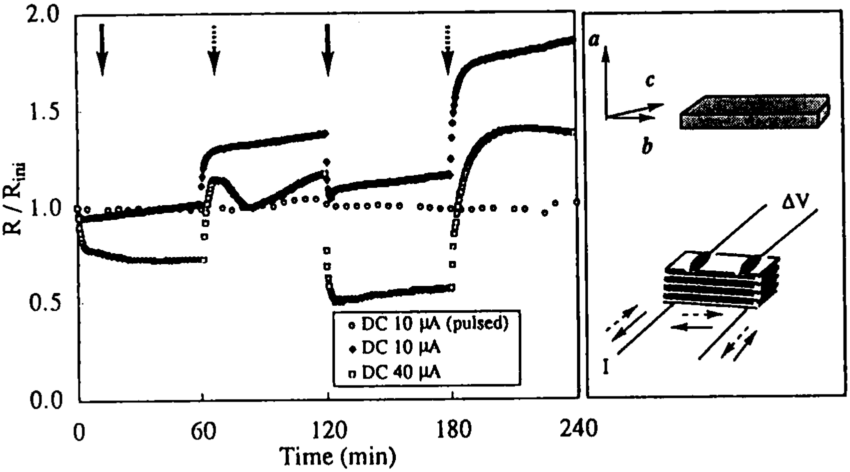

FIGURE 3 Dependence of the resistivity on the direction of the direct current (left) ; Direction of the direct current to the applied to the crystal (right)

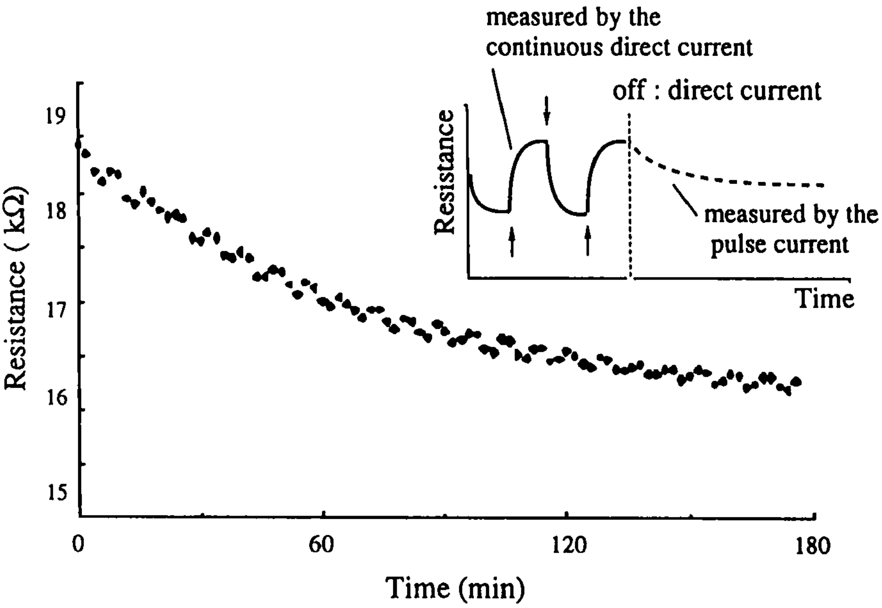

FIGURE 4 Decay curve of the resistivity of $(BEDT\text{-}TTF)_3Cl_2 \cdot 5H_2O$

How these unusual behaviors observed in the ET salt can be rationalized? One of the plausible mechanisms is shown in Figure 5. When the direct current is passed through the salt in order to measure the resistance of the salt, the electric field of ca. 10 ~ 50 mV is supposed to be applied to the crystal along this direction. Then, a sort of electric field-induced structural transition may take place in the hydrated chloride ion layer. In the absence of the external electric field, the location of the chloride ion is disordered between plural sites. The location, however, becomes ordered when the external electric field is applied, because one of the sites is stabilized under the electric field (Figure 5). In the low resistivity state, the stable location of the chloride ion maintains a homogeneous stacking and/or distribution of the positive charge along the donor column. While in the high resistivity stage, the location of the anion may causes the localization of the positive charge, disturbing the mixed-valent electronic state of the donor column. Such a migration of ions is presumably coupled by the change of the hydrogen-bonded scheme.

The dehydration process of the ion-radical salt was monitored by TG and DTA experiment. The first one water molecule was lost gradually in the temperature range of 30 ~ 53 °C and the next two water molecules were lost in a relatively narrow temperature range of 53 ~ 60 °C. The fourth water molecule was removed at around 70 °C. When the dependence of the rectifying effect was measured on the different hydration stages, the role of the water molecules is expected to become clearer.

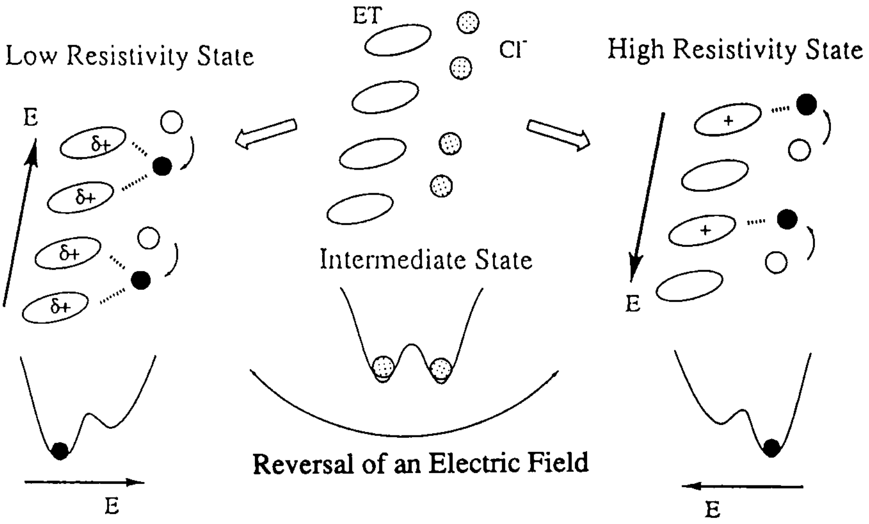

FIGURE 5 Plausible mechanism of rectifying effect of (BEDT-TTF)$_3$Cl$_2$•5H$_2$O (Filled circles represent the positions occupied by chloride ions under the external electric field. Open circles represent the vacancies. Dotted circles are for disordered sites.)

CONCLUSION

We have prepared a novel type of ET salts with a multi-layered structure. The salt consists of the organic donor layers and the inorganic counter ion layers involving hydrating water molecules. The salt was found to show a rectifying effect when the direction of the passing direct current was switched.

This phenomenon may be utilized to control the transport property by the external electric field. Namely the reversible external electric field is applied along the vertical direction to the transporting path, the transport property may be influenced significantly. Such a molecular system may have a possibility to be developed as a novel molecular devices as shown schematically in Figure 6.

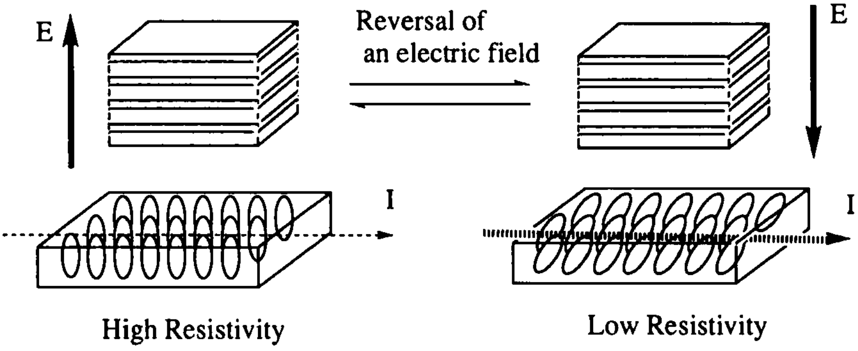

FIGURE 6 Control of resistivity by applying the external electric field

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