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Preparation and Properties of $(BEDT-TTF)_2Br\cdot 3H_2O$ Salt

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Abstract: Electrochemical oxidation of BEDT–TTF (bis (ethylenedithio) tetrathiafulvalene) in chloroform/carbon disulfide (3:1) in the presence of Bu_4NBr as a supporting electrolyte at low current density results in the $(BEDT-TTF)_2Br\cdot 3H_2O$ crystal. Its composition has been established by chemical analysis (Br, C, H, S), XPS and IR. The temperature dependence of the resistance has been studied down to 26K at ambient pressure. This material has weakly metallic behavior above 230K, and becomes a semiconductor below this temperature. The structure of the complex is also described.

Keywords: Organic conductor, charge transfer complex, preparation, electrical properties, structure.

Charge transfer salts of organic donor molecule bis (ethylenedithio) tetrathiafulvalene (BEDT–TTF) have been of great interest during the last decades, because of the wide range of physical properties which they exhibit [1, 2, 3]. Recently, our group prepared and studied organic conductors on the base of Ni $(dmit)_2$ anions (dmit = 1,3-dithiol-2-thione-4, 5-dithiolate) with EDA[4] (2-diethylamino-1, 3-dithiolanylium), and founded that there were many S···S contacts which are shorter than the sum of van der Waals radii (3.70Å) between cations and anions. The results prompted us to introduce rich S atoms into BEDT–TTF complex, hoping to form three dimensional S···S network and acquire good electrical conductivity. We tried to introduce CS_2 to BEDT–TTF salts in the presence of supporting electrolytes of Bu_4NBr, but found that the complexes did not contain CS_2. Instead, a new organic conductor was obtained.

In this paper, we report the preparation of $(BEDT-TTF)_2Br\cdot 3H_2O$ in the TBABr + CS_2 + $CHCl_3$ system.

Crystals were prepared by an electrochemical oxidation of 0.65 mmol/l BEDT–TTF solution in chloroform/carbon disulfide (3: 1) at a Pt anode at room temperature. D. C. current was less than 1 μA (0.8μ A). The supporting electrolyte is TBABr (62 mmol/l). After ten days black plate crystals were obtained. Elemental analysis $(BEDT-TTF)_2Br\cdot 3H_2O$: Calcd C% 26.61, H% 2.44, S% 56.77, Br% 8.86; Anal C% 26.51, H% 2.50, S% 56.73, Br% 8.73.

IR Spectral Analysis

A strong peak appearing at 3443 cm^{-1} in FT – IR spectra of $(BEDT – TTF)_2Br^{-}3H_2O$ shows the characteristic OH groups stretching band. The result indicates the presence of H_2O. Some other characteristic bands of νCH_2, C=C, C-S, δCH_2 bands in the $(BEDT – TTF)_2Br^{-}3H_2O$ complexes appear at 2897 cm^{-1}, 1631 cm^{-1}, 1340 – 1270 cm^{-1} and 1403 cm^{-1} respectively.

XPS Measurement

XPS spectra show that the salts contain Br atoms whose binding energy is 67.20 ev. The quantification of S (2p) and Br (3d) in the $(BEDT – TTF)_2Br^{-}3H_2O$ from XPS measure-ments are summarized in **Table 1.**

Table 1 Quantification of S (2p) and Br (3d) in the $(BEDT – TTF)_2Br^{-}3H_2O$

Peak	Center	SF	PK Area	T_x Function	Norm area	[AT]%
S_{2p}	164.24	1.74	2265.597	3548.1	0.00743	94.050
Br_{3d}	67.30	3.04	352.574	3548.1	0.00047	5.950

It can be seen that AT ratio of S (2p) and Br (3d) is 15.8 which is very close to 16. The XPS results suggest that there may have two BEDT – TTFs and one Br in one unit of the crystal.

Structure of $(BEDT – TTF)_2Br^{-}3H_2O$ crystal

The crystal structure of $(BEDT–TTF)_2Br^{-}3H_2O$ is shown in **Figure 1.** The crystallographic parameters are: $C_{20}H_{22}BrO_3S_{16}$; M=903.25; a=32.784 (6) Å, b=6.729 (2) Å, c=14.991 (4) Å; $\alpha=\alpha=\alpha=90^0$; V=3307.3 (12) Å; Space group P_{cca}. In the crystal of $(BEDT–TTF)_2Br^{-}3H_2O$, two BEDT-TTF molecules are in each unit cell, the ET molecules are stacked to form a column structure with overlapping along the c axis and sandwiched by Br^{-} and $3H_2O$ along the a axis. The intermolecular S···S contacts are shorter than van der Waals contacts.

Conductivity Measurement

The measurement of electric resistivity was performed by the conventional D.C. four-probe method. The contacts were applied by a gold paint and four gold wires were used as electrical leads. The room temperature conductivity of the crystal is $5.1\Omega^{-1}cm^{-1}$. The temperature dependence of the resistance for a typical sample is shown in **Figure 2**. During slow cooling of the sample, it retains weak metallic behavior to 230 K. Below the temperature it becomes semiconductor.

Figure 1 Crystal Structure of (BEDT – TTF)$_2$Br·3H$_2$O

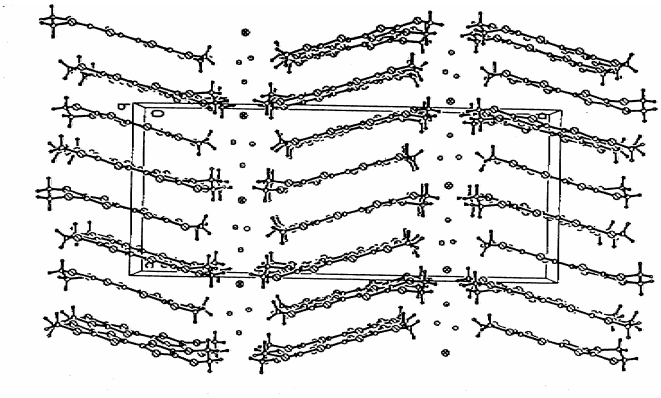
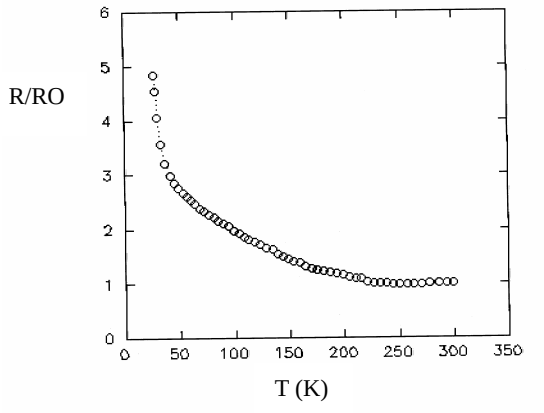


Figure 2. Temperature Dependence of Relative Resistance of (BEDT – TTF)$_2$Br·3H$_2$O



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