



Article Structures and Properties of New Organic Molecule-Based Metals, (D)₂BrC₂H₄SO₃ [D = BEDT-TTF and BETS]

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Abstract: An organic anion, 2-bromoethanesulfonate ($BrC_2H_4SO_3^-$), provides one bis(ethylenedithio) tetrathiafulvalene (BEDT-TTF) and two bis(ethylenedithio)tetraselenafulvalene (BETS) salts, the compositions of which are $\beta''-\beta''-(BEDT-TTF)_2BrC_2H_4SO_3$ (1), $\beta''-\beta''-(BETS)_2BrC_2H_4SO_3$ (2), and θ -(BETS)₂BrC₂H₄SO₃ (3), respectively. Compound 1 shows a metal–insulator transition at around 70 K. Compound 2 is isomorphous to 1, and 3 is polymorphic with 2. Compounds 2 and 3 show metallic behavior at least down to 4.2 K. The pressure dependence of the electrical resistivity of 1 is also reported.

Keywords: organic conductors; organic anions; electrocrystallization; crystal structure; band structure; electrical resistivity; magnetic susceptibility

1. Introduction

Over the past half century, numerous organic conductors have been prepared [1], particularly electron donor-anion type conductors, based on TTF (tetrathiafulvalene), TMTTF (tetramethyltetrathiafulvalene), TMTSF (tetramethyltetraselenafulvalene), BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene), BETS (bis(ethylenedithio)tetraselenafulvalene), etc., with a wide variety of counterions, which are commonly inorganic, such as BF_4^- , PF₆⁻, ClO₄⁻, Cl⁻, Br⁻, I⁻, I₃⁻, AuI₂⁻, etc. Organic anions, which are less common than inorganic ions, have also been used. The first radical cation salts with organic anions were reported by D. R. Rosseinsky et al. in 1979 [2], where CH₃CO₂⁻, maleate, fumarate, and p-MeC₆H₄SO₂⁻ were used. Each electrocrystallization with TTF gave powder, microcrystalline, or blocklets. However, the crystal structures were not determined. According to a review about the organic conducting salts with organic and organometallic anions [3], in 1983, the crystal structures of a $CF_3SO_3^-$ salt of TMTSF was reported [4]. However, $CF_3SO_3^-$ is not clearly organic because the anion includes no hydrogens. In 1985, the crystal structures of TMTTF and TTMTTF (tetramethylthiotetrathiafulvalene) salts with hexacyanobutadiene (HGBD) were reported [5]. However, HGBD was used not as an anion but as an electron acceptor because the crystals were obtained by mixing hot acetonitrile solutions of the donor and the acceptor, namely HGBD. This indicates that these are donoracceptor complexes. The crystal structure of the first organic conducting salt with an organic anion reported in 1988 by Peter Day's group [6] is $(BEDT-TTF)_2(p-CH_3C_6H_4SO_3)$. After the discovery, sulfonates were widely used as counterions of organic conductors [3,7–10] because sulfonates have relatively low pK_a (<1), which indicates that the bare monoanion state $(-SO_3^-)$ is far more stable than the protonated state $(-SO_3H)$. By contrast carboxylates $(-CO_2^{-})$ are not useful as counterions because of the relatively high pK_a (>3), where the protonated state ($-CO_2H$) is much more stable than the bare monoanion state ($-CO_2^{-}$). We have already reported several organic conducting salts with sulfonates [11–41], which are relatively large and anisotropic and several of which have provided unique salts having polar counterion layers [20,28,29,35,36,38,41]. Schematic diagrams of the crystal structures



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). of the salts are shown in Figure S1. Here we report new BEDT-TTF and BETS salts of a relatively small and anisotropic sulfonate, $BrC_2H_4SO_3^{-1}$.

2. Results and Discussion

A conventional constant-current electrocrystallization in a mixed solvent of PhCl (18 mL) and EtOH (2 mL) with BEDT-TTF (10 mg), BrC₂H₄SO₃Na (44 mg), and 18-crown-6 ether (67 mg) gave black blocks and thick needles. X-ray analyses indicated that the blocks and needles had the same cell parameters. The resulting data were solved as β'' - β'' -(BEDT- $TTF_{2}(BrC_{2}H_{4}SO_{3})$ (1). Using BETS (5 mg) instead of BEDT-TTF afforded dark green plates (3) with a small number of black blocks and needles (2). X-ray analyses indicated that 2 was isomorphous to 1, and the composition of the major product 3 was θ -(BETS)₂(BrC₂H₄SO₃), which is a polymorph of 2 and the cell parameters are different from those of 2. The crystallographic data of 1, 2, and 3 are shown in Table 1. Using $o-C_6H_4Cl_2$ (18 mL) instead of PhCl in the electrocrystallization of 1 yielded black thin plates (4), X-ray analysis of which indicated that the composition was (BEDT-TTF)₃(Br₃)₅, the structure and properties of which have already been reported [42]. This indicates that the $BrC_2H_4SO_3^-$ anion decomposed during the electrocrystallization process. Indeed, both the cell parameters and the crystal structure (Figure S2) were the same as reported in ref. [42]. However, the electrical resistivity measurement indicated that the salt 4 was metallic down to 4.2 K (Figure S3), whereas ref. [42] reported a broad metal-insulator (MI) transition at 120 K. The difference may be caused by a difference in the direction of the resistivity measurements and/or crystal conditions.

Compound	1	2	3	3	3
Formula	C ₂₂ H ₂₀ O ₃ S ₁₇ Br	C ₂₂ H ₂₀ O ₃ S ₉ Se ₈ Br	C ₂₂ H ₂₀ O ₃ S ₉ Se ₈ Br	C ₂₂ H ₂₀ O ₃ S ₉ Se ₈ Br	C ₂₂ H ₂₀ O ₃ S ₉ Se ₈ Br
Fw *1	957.32	1332.52	1267.52	1267.52	1267.52
Space Group	$P\overline{1}$	$P\overline{1}$	C2/c	C2/c	C2/c
a (Å)	5.8671(2)	5.93509(18)	35.850(2)	35.686(2)	35.633(2)
b (Å)	8.7790(2)	8.8364(2)	5.1587(3)	5.1193(3)	5.0986(4)
<i>c</i> (Å)	33.3201(7)	34.0428(9)	9.9900(6)	9.9154(7)	9.9154(7)
α (°)	89.076(6)	88.939(6)	90.0	90.0	90.0
β (°)	85.469(6)	85.697(6)	93.346(7)	92.695(7)	92.673(7)
γ (°)	75.793(5)	76.167(5)	90.0	90.0	90.0
V (Å ³)	1658.53(9)	1728.70(9)	1844.38(19)	1809.43(19)	1798.1(2)
Ζ	2	2	2	2	2
T(K)	150	150	290	150	110
$d_{\text{calc}} \left(\text{g} \cdot \text{cm}^{-1} \right)$	1.917	2.560	2.399	2.446	2.461
μ (cm $^{-1}$) * ²	23.434	101.896	95.505	97.349	97.963
$F(000) *^{3}$	966	1254	1254	1254	1254
2θ range (°)	4–55	4–55	4–55	4–55	4–55
Total ref.	16,127	16,694	8164	7936	8018
Unique ref.	7559	7871	2110	2081	2063
R _{int}	0.0325	0.0672	0.0733	0.0391	0.0431
Parameters	407	395	118	118	118
$R_1 \; (I > 2\sigma(I))$	0.032	0.049	0.063	0.051	0.059
wR_2 (all data)	0.089	0.158	0.205	0.138	0.166
S *4	1.009	1.042	1.060	1.119	1.088
Δho_{max} (e Å ⁻³)	1.49	1.94	1.18	2.18	2.20
Δho_{min} (e Å ⁻³)	-0.72	-1.73	-0.62	-1.92	-2.06
CCDC number	2 083 397	2 083 398	2 088 144	2 083 399	2 088 145

Table 1. Crystallographic data of 1, 2, and 3.

*1 Formula weight, *2 linear absorption coefficient, *3 total number of electrons in the unit cell, *4 goodness of fitness.

2.1. Crystal Structures

2.1.1. Crystal Structure of $\beta''-\beta''-(BEDT-TTF)_2(BrC_2H_4SO_3)$ (1)

Figure 1a shows the crystal structure of 1. Two BEDT-TTF molecules (A and B) and one $BrC_2H_4SO_3^-$ anion are crystallographically-independent. The unit cell has two independent donor layers, one of which consists of only the donor A (A layer) and the other of which consists of only the donor B (B layer). One of the two ethylene groups of A is disordered and refined over two positions, the refined occupancies of which are found to be 0.734 and 0.266. Both donor layers have quite similar β'' -type arrangements, as shown in Figure 1b,c. Each donor layer alternates with an anionic layer. Figure 1d shows short contacts between S atoms of BEDT-TTF molecules and O atoms of sulfo $(-SO_3^-)$ groups. In our previous reports, concerning sulfonate salts that are in the charge-ordered state, the donor having the shortest S…O contact with a sulfonate has the largest positive charge, perhaps because of the largest Madelung potential [20,31,35]. However, in salt 1, both A and B molecules have short S…O contacts, the distances of which are almost the same. This suggests that no charge disproportionation occurs. The molecular charges of A and B were estimated from bond lengths according to the literature method [43]. The calculated charges, normalized by the total formula charge (and non-normalized charge), are +0.492 (+0.567) and +0.508 (+0.586) for A and B, respectively. Both values are close to +0.5, suggesting no charge disproportionation. Figure 1e shows the structure of the anionic layer. All anions in the layer orient along the same direction (//b), which confers a dipole moment on the anionic layer. However, an inversion center provides the other anionic layer in the unit cell with the opposite dipole moment. Therefore, no net dipole moment exists. According to our classification suggested in ref. [44], the crystal has a Type III dipole arrangement (Figure S1) [44,45]. In addition, the dipole moment of the $BrC_2H_4SO_3^-$ anion was calculated by MOPAC7 [46] using the geometry observed in 1 to be 9.9 D.



Figure 1. (a) Crystal structure, donor arrangements of (b) A and (c) B layers with two crystallographically-independent plane–plane distances, where the dashed lines indicate S…S contacts shorter than the van der Waals distance of 3.70 Å, (d) short contacts between donors and anions, and (e) structure of the anion layer of **1**.

2.1.2. Crystal Structure of β'' - β'' -(BETS)₂(BrC₂H₄SO₃) (2)

As shown in Table 1, the cell parameters of **2** are almost the same as **1**, suggesting that both are isomorphous. Therefore, the crystal packing structure of **2** is not shown. There are two independent donors (A and B) and one anion in the asymmetric unit. Similar to **1**, one of the two ethylene groups of A is disordered and refined over two positions. The occupancies were found to be 0.799 and 0.201. Figure 2a,b shows the donor arrangements of both A and B layers, which are almost the same as 1. However, a larger number of short contacts were observed in A and B layers compared to 1, suggesting that 2 has stronger donor-donor interactions than 1. Figure 2c shows short contacts between S atoms of BETS molecules and O atoms of sulfo $(-SO_3^-)$ groups. An A molecule has a S…O contact that is 0.032 Å shorter than that of B. However, the difference is one order smaller than those of charge-ordered salts [20,31,35]. The relatively small difference suggests that the short anon–donor interactions provide no charge-ordered state. In addition, this cannot be confirmed since there are no previous studies on the relationship between bond lengths in BETS and the molecular charges. The molecular arrangement of the anionic layers of **2** is almost the same as **1**, and we do not show the structure. All anions in the layer orient along the same direction (//b) and therefore the crystal also has a Type III dipole arrangement [44,45]. In addition, the dipole moment of the $BrC_2H_4SO_3^-$ anion was calculated by MOPAC7 [46] using the geometry observed in 2 to be 9.7 D. In addition, a CCDC search indicated that the structures of 72 BETS salts have already been reported, which consist of 21 κ -, 18 θ -, 7 λ -, 7 α -, 4 β -, and 15 other miscellaneous types of salts. However, no β'' -type salts have been reported yet, indicating that **2** is the first BETS-based salt having a β'' -type donor arrangement.



Figure 2. Donor arrangements of (**a**) A and (**b**) B layers of **2** with two crystallographically-independent plane–plane distances, where the dashed lines indicate short Se…Se (<3.80 Å), Se…S (<3.75 Å), and S…S contacts (<3.70 Å). (**c**) Short contacts between donors and anions of **2**.

2.1.3. Crystal Structure of θ -(BETS)₂(BrC₂H₄SO₃) (3)

The thin plate crystals were the main products under the electrocrystallization condition, as mentioned previously. Figure 3a shows the molecular structure of the asymmetric unit of **3**. There are a half of BETS and a quarter of anion in the asymmetric unit. The donor is not disordered and located about the center of symmetry, whereas the anion is heavily disordered. The asymmetric part of the anion consists of -SO₃⁻, each occupancy of which is 0.25, and -CH₂CH₂Br disordered over two positions (-C61-C71-Br11 and -C62-C72-Br12), where each occupancy is 0.125. Thus, the anion is disordered over eight positions. Relatively large residual densities were observed due to the severe disorder. The asymmetric part of the anion is located about the center of symmetry, so that the anion layer is non-polar. The crystal structure is shown in Figure 3b. One donor layer and one anion layer are crystallographically-independent. Figure 3c shows the packing arrangement of the donor layer, which has a so called θ -type packing motif. The dihedral angle (θ) shown in Figure 3c of 98.1° was observed. A literature source [47] shows a phase diagram of the θ -type BEDT-TTF-based salts as a function of the dihedral angle (θ), where 98.1° is located in a superconducting phase. However, the salt **3** is BETS-based, not BEDT-TTF-based. BETS usually provides much stronger intermolecular interactions, which give much larger transfer integrals. Therefore, the interaction in **3** is stronger than that

of the BEDT-TTF-based salt, which suggests that **3** is a stable metal [48]. The occupancy of the BrC₂H₄SO₃⁻ anion of 0.25 suggests that there are four possible positions, one of which is occupied by an anion and the other three of which are vacant in the actual crystal. The anion is located about the center of symmetry, indicating that there are two possible positions on the inversion center. The length of the *b* axis of 5.1193(3) Å is too short for the anions to occupy each unit cell, suggesting that the anions exist every two-unit cells along the *b* axis. If anions exist in every two-unit cells regularly, which makes the length of the *b* axis double, the crystal usually provides satellite reflections and/or diffuse streaks on the X-ray photographs. No satellite reflections and/or diffuse streaks were observed in all 44 measured photographs. The lack of any superstructures suggests that the disorder is not so simple that each anion chain has unique periodicity. Furthermore, each donor, which also can form a superstructure of a $2k_F$ (four-fold) or $4k_F$ (two-fold) charge–density wave, gathers not to form any superstructures but to form a uniform stack. This again suggests that the salt is a stable metal.



Figure 3. (a) Molecular structure of the asymmetric unit, (b) crystal structure, and (c) packing motif of the donor layer with one independent plane–plane distance and dihedral angle of **3** at 150 K.

2.2. Electrical Resistivity

Temperature dependences of electrical resistivities of **1**, **2**, and **3** are shown in Figure 4. The BEDT-TTF salt **1** shows a metal–insulator (MI) transition at around 70 K, and then the resistivity gradually increases, and the resistivity at 4.2 K is 20 times larger than that at 70 K. β "-salts can be classified into several groups according to structural features [49]. According to the classification, **1** belongs to the β "₂₁₁-type. Most β "₂₁₁-salts are stable metals apart from the two salts, (BEDT-TTF)₂Br₂SeCN and (BEDT-TTF)₂Cl₂SeCN, which show relatively sharp MI transitions at 200 K. The isomorphous BETS-based salt **2** shows metallic behavior from room temperature down to 4.2 K. Salt **3** also shows metallic behavior across the whole temperature range.



Figure 4. Temperature-dependent electrical resistivities of 1, 2, and 3.

2.3. Magnetic Susceptibility

Temperature dependences of magnetic susceptibility of 1 and 3 are shown in Figure 5a,b, respectively. We have not yet obtained a sufficient quantity of 2 for SQUID measurement, and therefore the susceptibility data of **2** is not available. The magnetic susceptibility of **1** decreases monotonically from room temperature (RT) from 6 to 2×10^{-4} emu mol⁻¹, which are in the range of normal Pauli paramagnetism of organic BEDT-TTF-based metals [50], and then shows a more rapid decrease in susceptibility at the same temperature as was observed (70 K) for the metal-insulator (MI) transition. The susceptibility then becomes almost zero at the lowest measured temperature. The result indicates a non-magnetic ground state for **1**. Most β "-salts have charge-ordered ground states, suggesting that the ground state of 1 has a non-magnetic 0011 type of charge-ordered pattern [1]. We will discuss further this in the context of the electronic structure of **1** later. The susceptibility of **3** (Figure 5b) is almost constant, $\approx 2.5 \times 10^{-4}$ emu mol⁻¹, from RT to 175 K. On further lowering the temperature, the susceptibility decreases monotonically down to 2 K. The non-zero susceptibility, $\approx 1.2 \times 10^{-4}$ emu mol⁻¹, at the lowest temperature suggests that the sample has an itinerant nature down to 2 K. In addition, the ρ -T plot of 3 (Figure 5c) has an anomaly at 175 K, at which temperature the susceptibility starts decreasing, suggesting that there is a transition between two metallic phases at around 175 K. The temperature dependence of magnetic susceptibility of θ -(BETS)₂Cu₂Cl₆ [51], which is also a stable metal with $\theta = 100^{\circ}$, is similar to that of **3**. The broad decrease was observed from 2.3×10^{-4} above 120 K, where a structural phase transition (*Pbcn to* $P2_12_12$) is observed, to 1.0×10^{-4} emu mol $^{-1}$ below 70 K. X-ray analyses of 3 at 110 and 290 K were also performed (Table 1) to confirm whether there is a phase transition at around 175 K. However, cell parameters at 110 and 290 K are almost the same, and no structural phase transition was observed. The origin is not clear at present.



Figure 5. Temperature dependences of magnetic susceptibilities of (**a**) **1** and (**b**) **3**, where 0.46 and 0.30% of Curie tails have been subtracted, respectively. (**c**) Resistivity–temperature plots of **3**.

2.4. Band Structure Calculations

Band structures of 1, 2, and 3 were calculated using the Mori's band structure calculation software package [52]. The resultant overlap integrals are shown in Table 2. Figure 6 shows a schematic diagram of the donor layers with the directions and labelling of donordonor interactions. The p1 values of both A and B layers in 1 is one and two orders larger than those of p2, respectively, indicating strong dimerization along the stacking direction in each layer, which is also confirmed by the intermolecular spacing; the plane–plane distances of p1 are 0.167 (A layer) and 0.226 Å (B layer) shorter than those of p2 (see Figure 1b,c). The side-by-side interactions (r1, r2, and s) were larger than p1, suggesting that the salt is metallic along the side-by-side directions. Band dispersions and Fermi surfaces of 1 are shown in Figure 7a. There are quasi-1D electron sheets and hole pockets in the first Brillouin zone. The Fermi surface is open along the stacking direction (//b), suggesting that the metallic tendency along the side-by-side directions is stronger than that along the stacking direction. As previously described, the salt shows a MI transition, for which we speculate that a tetramerization along the side-by-side direction occurs (perhaps in the s direction because s values of A and B are the largest). The tetramerization will make the salt a band insulator to give a diamagnetic ground state, which is consistent with the magnetic behavior shown in Figure 5a. In addition, since the A and B layers of 1 have almost the same donor arrangements and overlap integrals (Table 2), both band dispersions and Fermi surfaces are also quite similar.

Salts 1 2 Layers Α В А В p1-5.03-4.88-6.43-5.97p2 -0.36-0.06+2.53+3.50r1-9.80-9.89-17.73-17.27r2 -10.74-9.60-18.70-16.87-14.50-14.98-26.02-26.96S

Table 2. Overlap integrals ($\times 10^{-3}$) of **1** and **2** at 150 K.



Figure 6. Schematic diagram of the structure of the donor layer with directions of interactions of **1** and **2**.

Similarly, the band dispersions and Fermi surfaces of A and B layers of **2** are also similar (Figure 7b) because, again, both layers have almost the same donor arrangements. Since **1** and **2** are isomorphous, their electronic structures are almost the same as compared in Figure 7a,b. However, **2** does not show a MI transition. The most significant difference between **1** and **2** is a degree of dimerization along the *b* axis. The values of |p1|/|p2| of **1** are 14.0 and 81.3 for A and B layers, respectively, but the similar values for **2** are only 2.5 and 1.7 for A and B layers, respectively. The considerably smaller values for **2** suggest that the support for dimerization in **2** is far weaker than in **1**, which is not reflected in the intermolecular spacing. The plane–plane distances of *p*1 are 0.205 (A layer) and 0.257 Å (B layer) shorter than those of *p*2 (see Figure 2a,b). The differences in **2** are rather larger than those in **1**. The weak dimerization in **2** makes carriers less correlated and stabilizes the metallic state. In addition, the band width of the conduction bands of **2** are 1.77 eV, which is 1.9 times larger than that of the 0.93 eV of **1**.

The donor arrangement of **3** is simple so that there are only two crystallographicallyindependent overlap integrals, one of which (*p*) lies along the stacking direction, and the other (*r*) lies along the side-by-side direction, as shown in Figure 3c. Values of p = 3.26 and $r = 22.52 \times 10^{-3}$ were calculated. Figure 8 shows the band dispersions and Fermi surfaces



of **3**. There is a simple and large 2D Fermi surface in the first Brillouin zone, and the band width of 1.80 eV was observed.

Figure 7. Band dispersions (left) and Fermi surfaces (right) of 1 (a) and 2 (b) at 150 K.



Figure 8. Band dispersions (left) and Fermi surfaces (right) of 3 at 150 K.

2.5. Electrical Resistivity under Pressure

For compound **1**, the electrical resistivity under static pressure up to 0.5 GPa (5.0 kbar) was measured. This was achieved using a clamp-type pressure cell from RT to 4.2 K (Figure 9). Applying 1.0 kbar of pressure made the MI transition sharper and moved the transition temperature ($T_{\rm MI}$) 10 K higher to 80 K. By contrast the 2.0 kbar curve reveals an upturn at 55 K, which is 15 K lower than that at 1 bar, but the transition is still sharper than that at 1 bar. The $T_{\rm MI}$ at 3.0 kbar is 51 K, which is only 4 K smaller than that at 2.0 kbar; however, the resistivity at 4.2 K ($\rho_{4.2 \rm K}$) is more than two orders of magnitude smaller than that at 2 kbar. In fact, $\rho_{4.2 \rm K}$ decreases with increasing pressure from 3 to 5 kbar. The upturn for the MI transition almost disappears at 4.5 kbar, but we have not yet observed superconductivity at the measured pressures and down to 4.2 K.



Figure 9. Electrical resistivity under pressure of 1.

3. Materials and Methods

BEDT-TTF, purchased from Tokyo Chemical Industry Co. Ltd., Tokyo, Japan, and BrC₂H₄SO₃Na, purchased from FUJIFILM Wako Pure Chemical Corporation (Chuo-Ku Osaka, Japan), were used without purification. 18-Crown-6 ether was used after recrystallization from acetonitrile. PhCl, purchased from Kishida Chemicals, was distilled from P₂O₅. EtOH, special grade, purchased from Kishida Chemicals, and *o*-C₆H₄Cl₂, HPLC grade, purchased from FUJIFILM Wako Pure Chemical Corporation, were used without further purification. Electrocrystallization was performed using a conventional H-shaped cell with Pt wire (1 mm ϕ) electrodes, between which 0.9 μ A for 20 days and 0.2 μ A for 2 months were applied for BEDT-TTF and BETS salts, respectively.

Single crystal X-ray measurements were performed at 150 K for 1 and 2 and at 110, 150 and 290 K for 3 with a Rigaku Rapid II imaging plate system with MicroMax-007 HF/VariMax rotating-anode X-ray generator with confocal monochromated MoK α radiation. The crystallographic data of 1, 2, and 3 are listed in Table 1. The structures of 1, 2, and 3 were solved by SHELXT [53], and each structure refinement was completed with SHELXL [53] software. The intensities were corrected for absorption with ABSCOR (Higashi, T. (1995); ABSCOR. Rigaku Corporation, Tokyo, Japan). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. The disordered ethylene moieties in 1 and 2 were constrained displacement parameters (EADP in SHELX). The anion in **3** was severely disordered and refined with bond distance and angle restraints (DFIX and DANG in SHELX) and constrained displacement parameters (EADP in SHELX). In the circumstance, relatively large residual densities were observed. In addition, 1 and 2 salts had relatively weaker reflections with h + l = odd than those with h + l = even, suggesting the possibility that the cell volumes become half. Actually, **1** and **2** can be solved using the cell parameters with the half volumes, **1'**: $P\overline{1}$, a = 5.8667(2), b = 8.7788(2), c = 16.6858(5) Å, $\alpha = 88.451(6)$, $\beta = 84.438(6)$, $\gamma = 75.791(5)^{\circ}$, V = 829.14(5) Å³, $R(I > 2\sigma(I)) = 3.0\%$, wR(all data) = 8.1%, $R_{int} = 3.2\%$, and 2': $P\overline{1}$, a = 5.9343(2), b = 8.8354(3), c = 17.0567(5) Å, $\alpha = 88.674(6)$, $\beta = 84.312(6)$, $\gamma = 76.164(5)^{\circ}$, $V = 864.09(5) \text{ Å}^3$, $R(I > 2\sigma(I)) = 3.9\%$, wR(all data) = 11.6%, $R_{\text{int}} = 6.4\%$. Each asymmetric unit has one donor and a half of anion, the latter of which is located about a center of symmetry and which is disordered where Br atoms and crystallographically-independent SO_3 group are overlapped. Only one donor layer is crystallographically-independent in 1' and **2'**. However, **1** and **2** have many reflections with h + l = odd, which were significantly observed ($I >> 3\sigma(I)$). For example, the intensity (I), sigma (σ), and $I/\sigma(I)$ of (-22-7) of 236.10, 3.04, and 77.66, respectively, for 1 and 123.45, 2.20, and 56.11, respectively, for 2 were observed. Moreover, 1' and 2' have the disorder of the anion, which does not exist in 1 and 2. Therefore, we decided that 1 and 2 are correct. The relatively low *R* values of 1' and 2' indicate that each salt has pseudosymmetry because the structures of each two independent donor layers are quite similar in 1 and 2. Electrical AC resistivity measurements from 4.2 to 300 K were measured by the conventional four-probe method using a HUSO HECS 994C1 four channel resistivity meter with cooling and heating rates of ≈ 0.5 K/min. Each resistivity value was recorded after averaging for 10 s. Temperature-dependent magnetic susceptibility of a polycrystalline sample from 2 to 300 K was measured using a Quantum Design MPMS-2S SQUID magnetometer. The magnetic susceptibility data of 1 and 3 were corrected for a contribution from an aluminum foil sample holder, and the diamagnetic contributions of the samples were estimated from Pascal's constant (-4.444and -5.084×10^{-4} emu mol⁻¹ for 1 and 3, respectively). The contributions of the Al foil sample holders were of the same orders as those of conducting electrons. Due to the relatively low contribution of the conducting electrons, less than 20% of absolute error was sometimes observed.

4. Conclusions

We prepared three new BEDT-TTF- and BETS-based organic conductors with an organic sulfonate anion, bromoethanesulfonate, $\beta''-\beta''-(BEDT-TTF)_2BrC_2H_4SO_3$ (1), $\beta''-\beta''-(BETS)_2BrC_2H_4SO_3$ (2), and θ -(BETS)_2BrC_2H_4SO_3 (3). Salt 1 shows a MI transition at around 70 K. The isomorphous 2 does not show a MI transition and is metallic down to at least 4.2 K. Compound 3 is also a stable metal down to at least 4.2 K. The dihedral angle of 3 of 98.1° is located in the superconducting phase of the phase diagram of the θ -type BEDT-TTF salts. This suggests that if we can obtain the isomorphous BEDT-TTF-based salt, it may show superconductivity (a resistivity drop and a Meissner effect). Preparation of the θ -type BEDT-TTF salt is now in progress.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/ 10.3390/magnetochemistry7070091/s1, Figure S1. Schematic diagrams of the crystal structures of Type I-IV salts where the electrical di-poles of the counterions are indicated by arrows, electrically conducting layers are shown as green squares, and counterion layers are shown as blue rectangles, Figure S2. Crystal structure of 4, Figure S3. Temperature-dependent electrical resistivity of 4.

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