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BEDT-TTF Tris(oxalato)germanate(IV) Salts with Novel Donor Packing Motifs

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The synthesis, crystal structure, and conducting properties of two new BEDT-TTF charge-transfer salts containing tris(oxalato)germanate(IV) anions are described. (BEDT-TTF)$_5$[Ge(C_2O_4)$_3$]$_2$ (**1**) crystallizes in the monoclinic space group $C2$, $a = 23.0994(11)$ Å, $b = 11.0200(5)$ Å, $c = 19.5455(9)$ Å, $\beta = 117.628(4)°$, $V = 4408.1(4)$ Å^3, $T = 120(2)$ K, $Z = 2$, $R1 = 0.0659$ [$F^2 > 2\sigma(F^2)$]. Compound **2** (BEDT-TTF)$_7$[(Ge(C_2O_4)$_3$]$_2$•0.87CH_2Cl_2•0.09H_2O crystallizes in the monoclinic space group $C2/c$, $a = 37.081(2)$ Å, $b = 11.5449(7)$ Å, $c = 28.6415(13)$ Å, $\beta = 93.7767(9)°$, $V = 12234.8(12)$ Å^3, $T = 293(2)$ K, $Z = 4$, $R1 = 0.0834$ [$F^2 > 2\sigma(F^2)$]. Electrical resistivity measurements show that **1** and **2** are both semiconductors.

The organic chalcogenide donor molecule BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene] has produced a large number of conducting materials with a diverse range of electronic ground states because the BEDT-TTF molecules can adopt a variety of packing motifs.[1] For example, the series of charge-transfer salts (BEDT-TTF)$_4$[(A)M^{3+}(C_2O_4)$_3$]•solvent includes superconductors, metals, semiconductors, and insulators depending on the donor packing mode.[2] The packing motif of the organic donor layer is determined by close atomic contacts with the tris(oxalato)metallate layer.[3] Changing the metal (Fe^{3+}, Cr^{3+}, and Ga^{3+}) leads to a change in the superconducting T_c,[4] while changing A (H_3O^+, K^+, NH_4^+, and Na^+)[5] or changing the solvent (e.g., benzonitrile, pyridine, 1-phenylethanol, chlorobenzene, and DMF) can lead to changes between electronic ground states, produce multilayered materials and has even produced an ionic conductor.[6] Salts in this series can also be either superconducting or semiconducting depending on the distribution of Δ and Λ enantiomers of $[M(C_2O_4)_3]^{3-}$ within the tris(oxalato)metallate layer giving β'' or pseudo-κ packing, respectively.[7]

There has been only one previous example of changing the metal center from M^{3+} to M^{4+}: in (BEDT-TTF)$_2$Ge(C_2O_4)$_3$•C_6H_5CN[8] the structure is markedly different from that of the BEDT-TTF–M^{3+} salts and does not contain alternating layers of BEDT-TTF cations and tris(oxalato)metallate(III) anions, but instead is a checkerboard arrangement of face-to-face BEDT-TTF dimers interspersed with tris(oxalato)germanate(IV) with solvent molecules occupying a separate layer to the anions and cations. In contrast, crystal engineering of the series containing tris(oxalato)metallate(III) has been studied extensively.[2–7] Changing the guest molecule yields a large family of compounds, all with hexagonally packed anion layers. An important crystal engineering aspect we report here is that when the metal is M^{4+}, rather than M^{3+}, changing the guest molecule leads to drastic changes in the packing mode of both the anion and the cation layers. This paper reports two new molecular conducting salts containing tris(oxalato)germanate(IV) which both have BEDT-TTF packing motifs not observed before.

Experimental

Synthesis and Purification of Starting Materials. Ammonium tris(oxalato)germanate[9] was prepared from germanium oxide (1.67 g), ammonium oxalate (1.83 g), and oxalic acid (4.04 g) which was refluxed until all the solids had dissolved in 75 mL of H_2O. Upon cooling to 40 °C, 90% ethanol (80 mL) was added to precipitate the ammonium tris(oxalato)germanate upon further cooling. The crystals were washed with ice cold water/ethanol (50:50). The crude product was dissolved in H_2O (30 mL) at 70 °C, 95% ethanol (30 mL) was added and the solution was allowed to cool to room temperature. Large white crystals formed and were washed with ice cold ethanol (25 mL), then ice cold ether (25 mL) and dried. BEDT-TTF (Fluka) was recrystallized three times from chloroform. 18-Crown-6 (Aldrich) was dried over acetonitrile. The solvents used (acetophenone, dichloromethane, and acetonitrile; Aldrich) were distilled immediately prior to electrocrystallization.

Electrocrystallization. Three-compartment H-shaped cells with a volume of 40 mL were used to grow crystals of (BEDT-TTF)$_5$[Ge(C_2O_4)$_3$]$_2$ (**1**) and (BEDT-TTF)$_7$[(Ge(C_2O_4)$_3$]$_2$•0.87CH_2Cl_2•0.09H_2O (**2**) by electrocrystallization. Each cell has two platinum electrodes, separated by two porous glass frits to prevent contamination by reduction products. The electrodes were cleaned by washing in concentrated HNO_3 followed by applying a voltage across the electrodes in 1 M H_2SO_4 in each direction until the evolution of H_2 and O_2 at the electrodes. Finally the electrodes

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Table 1. Crystal Data for **1** and **2**

Compound	**1**	**2**
Empirical formula	$C_{62}H_{40}Ge_2O_{24}S_{40}$	$C_{82.87}H_{57.91}Ge_2Cl_{1.73}O_{24.09}S_{56}$
Formula weight	2596.52	3441.02
Temperature/K	120(2)	293(2)
μ/mm^{-1}	1.704	1.552
Radiation λ/Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	*C*2	*C*2/*c*
a/Å	23.0994(11)	37.081(2)
b/Å	11.0200(5)	11.5449(7)
c/Å	19.5455(9)	28.6415(13)
α/°	90	90
β/°	117.628(4)	93.7767(9)
γ/°	90	90
V/Å^3	4408.1(4)	12234.8(12)
Z	2	4
ρ/Mg m^{-3}	1.956	1.868
Reflections collected	32351	41015
Independent reflections	10017	11853
Data/restraints/parameters	10017/924/741	11853/0/797
*R*1 [$F^2 > 2\sigma(F^2)$]	0.0659	0.0834
*wR*2	0.1356	0.0875

were washed in distilled water and thoroughly dried. The cells were fixed inside sand-filled compartments on a concrete table, to minimize vibration and were kept at a constant temperature of 293(2) K and a constant current source was used to control the crystal growth rate.

Electrocrystallization of (BEDT-TTF)$_5$[Ge(C$_2$O$_4$)$_3$]$_2$ (1). 120 mg of $(NH_4)_2[Ge(C_2O_4)_3]\cdot 2H_2O$ and 250 mg of 18-crown-6 ether in 40 mL of (*R*)-(−)-carvone with 3 drops of H_2O was stirred overnight and filtered into an electrochemical cell containing 10 mg of ET in the anode compartment. On applying a current of 0.2 µA across the cell for one week a large quantity of black needle-shaped crystals of (BEDT-TTF)$_5$[Ge(C$_2$O$_4$)$_3$]$_2$ (**1**) were obtained (average size 0.16 × 0.04 × 0.02 mm^3) and were found to be suitable for X-ray structure determination (Table 1).

Crystal data **1**: $C_{62}H_{40}Ge_2O_{24}S_{40}$, $M_r = 2596.52$, black lath, monoclinic, $a = 23.0994(11)$ Å, $b = 11.0200(5)$ Å, $c = 19.5455(9)$ Å, $\alpha = 90°$, $\beta = 117.628(4)°$, $\gamma = 90°$, $V = 4408.1(4)$ Å^3, $T = 120(2)$ K, space group *C*2, $Z = 2$, $\mu = 1.704$ mm^{-1}, reflections collected = 32351, independent reflections = 10017, $R1 = 0.0659$, $wR2 = 0.1356$ [$F^2 > 2\sigma(F^2)$], $R1 = 0.1010$, $wR2 = 0.1549$ (all data), absolute structure parameter 0.43(3).

Diffractometer: Nonius KappaCCD area detector (ϕ scans and ω scans to fill asymmetric unit sphere). Cell determination: DirAx,[10] Data collection: Collect,[11] Data reduction and cell refinement: Denzo,[12] Absorption correction: SADABS Version 2.10,[13] Structure solution: SHELXS97,[14] Structure refinement: SHELXL97,[15] Graphics: ORTEP3 for Windows.[16] All hydrogen atoms were fixed. The oxalates were disordered over 2 sites. Due to the disorder of the oxalate anions, each oxalate was restrained to have the same basic geometry. There was a global DELU thermal restraint used on all atoms so that neighboring atoms had similar thermal parameters, again employed due to the disorder of the oxalate.

Electrocrystallization of (BEDT-TTF)$_7$[(Ge(C$_2$O$_4$)$_3$]$_2$·0.87CH$_2$Cl$_2$·0.09H$_2$O (2). 120 mg of $(NH_4)_2[Ge(C_2O_4)_3]\cdot 2H_2O$ and 250 mg of 18-crown-6 ether in 40 mL of freshly distilled dichloromethane with 3 drops of H_2O was stirred overnight and filtered into an electrochemical cell containing 10 mg of ET in the anode compartment. On applying a current of 1.0 µA across the cell, crystals began to grow in the first week and were harvested after two weeks. A large quantity of black rhombus-shaped crystals of (BEDT-TTF)$_7$[(Ge(C$_2$O$_4$)$_3$]$_2$·0.87CH$_2$Cl$_2$·0.09H$_2$O (**2**) were obtained (average size 0.45 × 0.45 × 0.05 mm^3) and were found to be suitable for X-ray structure determination (Table 1).

Crystal data **2**: $C_{82.87}H_{57.91}Ge_2Cl_{1.73}O_{24.09}S_{56}$, $M_r = 3441.02$, black rhombus, monoclinic, $a = 37.081(2)$ Å, $b = 11.5449(7)$ Å, $c = 28.6415(13)$ Å, $\alpha = 90°$, $\beta = 93.7767(9)°$, $\gamma = 90°$, $V = 12234.8(12)$ Å^3, $T = 293(2)$ K, space group *C*2/*c*, $Z = 4$, $\mu = 1.552$ mm^{-1}, reflections collected = 41015, independent reflections = 11853, $R1 = 0.0834$, $wR2 = 0.0875$ [$F^2 > 2\sigma(F^2)$].

Diffractometer: Quantum-1 CCD/Rigaku AFC-7R ϕ and ω scans to fill asymmetric unit sphere. Cell determination: DTREK. Data collection: Rigaku Diffractometer Controller. Data reduction and cell refinement: DTREK. Absorption correction: ABSCOR.[17] Structures were solved by direct methods (SIR92[18]) and refined anisotropically (CrystalStructure Ver 3.8.2[19]). All hydrogen atoms were allowed to ride on their respective parent atoms.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-741057 and -741058 for compounds **1** and **2**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Physical Measurements. Raman spectra were recorded at room temperature with a Renishaw InVia Raman microscope equipped with a diode laser (785 nm) and a 1200 L mm^{-1} grating using a laser power of ca. 1 mW. The recorded spectra are the result of 20 accumulations of 5 s each from 1200 to 1650 cm^{-1} to observe the BEDT-TTF ν_3 and ν_4 wavenumbers.

Four-probe DC transport measurements were made on several crystals of **1** and **2** using a HUSO HECS 994C multi-channel conductometer. Gold wires (15 µm diameter) were attached to the crystal, and the attached wires were connected to a four-pin circuit plug with gold conductive cement. Reproducible transport measurements were measured along the *b* axis for **1** and in the *bc* conducting plane for **2**.

Structure Determination. The crystallographic data collection of **1** was performed using a Nonius KappaCCD diffractometer with Mo Kα radiation and an Oxford Cryosystem N$_2$ open flow cryostat at 120(2) K. The crystallographic data collection of **2** was performed using a Quantum CCD/AFC-7R diffractometer at 293(2) K.

Results and Discussion

Crystal Structures. Compounds **1** and **2** crystallize in the space groups *C*2 and *C*2/*c* respectively. The structures **1** and **2** differ greatly from those found with BEDT-TTF and tris(oxalato)metallate(III). When using $[M(C_2O_4)_3]^{3-}$ (M = Cr^{3+}, Fe^{3+}, Co^{3+}, Al^{3+}, or Ga^{3+}) the anion usually forms a hexagonal packing arrangement with molecules of NH$_4^+$, H$_3$O$^+$, K$^+$, or Na$^+$ giving the anion layer a charge of 2− in these salts. The same 2− charge is found for the anion layers in **1** and **2** where $[Ge(C_2O_4)_3]^{2-}$ is present without the presence of a monopositive counter cation. Despite the anion layers in both systems having the same 2− valence, hexagonal packing has not been observed in the three salts found so far from BEDT-TTF with $[Ge(C_2O_4)_3]^{2-}$.[8] The structure of **1** also differs from

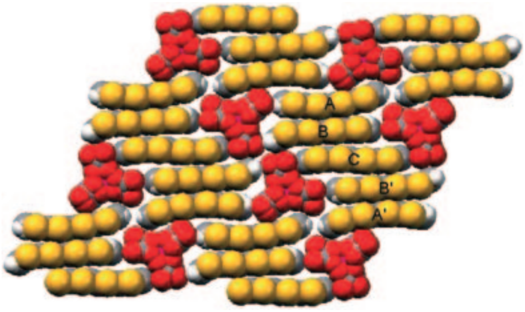

Figure 1. The structure of **1** viewed down the *b* axis. Carbon, grey; sulfur, yellow; oxygen, red; germanium, pink; hydrogen, white.

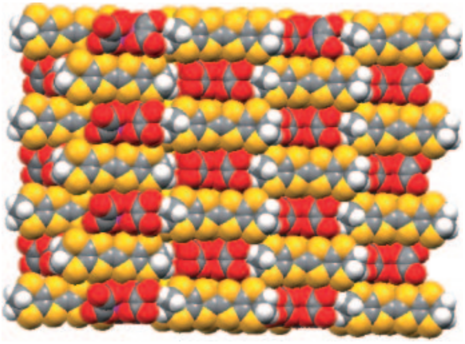

Figure 2. The structure of **1** viewed down the *c* axis. Carbon, grey; sulfur, yellow; oxygen, red; germanium, pink; hydrogen, white.

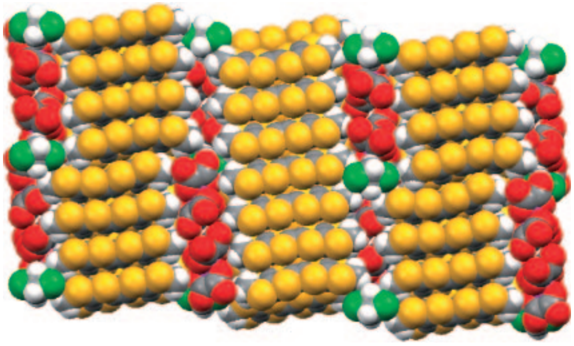

Figure 3. The structure of **2** viewed down the *b* axis. Carbon, grey; sulfur, yellow; oxygen, red; germanium, pink; chlorine, green; hydrogen, white.

the majority of charge-transfer salts of BEDT-TTF in that it has no alternating organic layers of BEDT-TTF and inorganic layers of the anion. We observe two unique packing arrangements of BEDT-TTF molecules.

The asymmetric unit of **1** contains two and a half BEDT-TTF molecules (A, B, and C in Figure 1), one tris(oxalato)germanate anion and no solvent molecules. There are no discrete anion and cation layers, which results in a novel packing arrangement of BEDT-TTF molecules (Figure 1). The BEDT-TTFs form diagonal stacks of five molecules, with a crystallographically unique molecule (C) sandwiched between two pairs of dimers (A–B and A′–B′ in Figure 1).

There are 3 short contacts between oxalate oxygens and hydrogens on the monomer BEDT-TTF molecule (C–H22B···O31 2.39(1) Å, C–H21B···O42 2.65(1) Å, and C–H21A···O43 2.07(1) Å), and 4 short contacts between oxalate oxygens and hydrogens on dimer BEDT-TTF molecules (C–H12A···O33 2.71(1) Å, C–H11B···O34 1.95(1) Å, C–H19B···O43 2.37(1) Å, and C–H10A···O44 2.46(1) Å).

Between the two dimer pair molecules there are face-to-face close S···S contacts (S4···S14 3.49(1) Å and S3···S13 3.48(1) Å) and also side-to-side contacts (S2···S8 3.51(1) Å, S12···S18 3.38(1) Å, S1···S7 3.51(1) Å, and S11···S17 3.32(1) Å). On the other hand the BEDT-TTF molecule which is not forming a dimer has only one close S···S contact (S21···S22 3.27(1) Å) which is side-to-side with a crystallographically equivalent molecule. One BEDT-TTF molecule of the dimer pair (A) has a boat conformation at one end and a twisted conformation at the other while the other (B) has a boat conformation at both ends on the same side of the TTF plane. A boat conformation is when both ethylene carbon atoms are on the same side of the central TTF plane while the twisted conformation has one carbon atom of the ethylene unit on either side of the plane.

The donor molecule which does not form a dimer (C) is in a boat–boat conformation with one ethylene group above and one below the TTF plane. Figure 2 shows the packing of the cations and anions in the *c* direction. The dimer pair BEDT-TTF molecules are positioned side-to-side with the tris(oxalato)germanate. As a result the boat–boat dimer BEDT-TTF molecule is bent from planarity at both ends probably as a result of steric interaction with the neighboring oxalate ligands in the anion.

Chirality of the anion is of particular interest in the series of salts of BEDT-TTF with tris(oxalato)metallate. It has been shown that the packing mode of the BEDT-TTF and thus the electronic ground state is determined by the spatial distribution of Δ and Λ enantiomers of the anion. In **1** there are no discrete anion layers and the crystal structure shows that each Ge site is disordered between the Δ and Λ enantiomer. A Flack parameter of 0.43(3) is observed which indicates an excess of one enantiomer of $[Ge(C_2O_4)_3]^{2-}$ and that **1** is a non-symmetric chiral conductor. We have demonstrated previously that the use of (*R*)-(−)-carvone when preparing BEDT-TTF tris(oxalato)-metallate salts results in chiral induction, i.e., crystallization of a chiral salt from a racemic precursor.[20]

The asymmetric unit of **2** contains three and a half BEDT-TTF molecules, a tris(oxalato)germanate anion, and CH_2Cl_2/H_2O molecules. Compound **2** consists of discrete anion and cation layers but incorporating an anion with charge 2− leads to an α-type packing arrangement of BEDT-TTF molecules (Figure 3). The BEDT-TTF molecules form blocks of seven molecules in a stack. Each block of seven BEDT-TTFs stacks in the *c* direction with the next stack shifted in the *a* direction with it's central TTF C=C bond over the six-membered ring of a BEDT-TTF in the previous stack (Figure 4). Each adjacent stack of BEDT-TTF (in the *b* direction) is displaced by 3.5 BEDT-TTFs in the *c* direction so that half of the BEDT-TTFs in a stack are side-to-side while the other half are displaced with their central TTF C=C bond over the six-membered ring of the BEDT-TTF in the adjacent stack (Figure 4). The BEDT-TTFs on the ends of each stack of seven have a boat–boat conformation while the remaining five BEDT-TTFs have

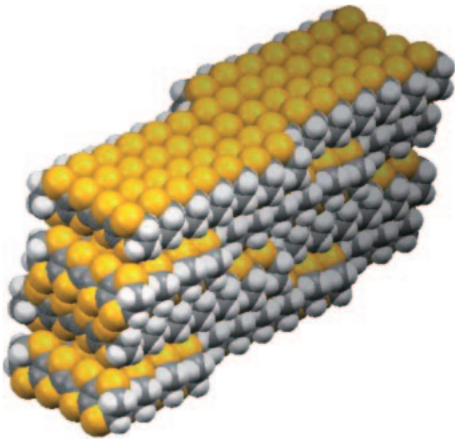

Figure 4. Packing of ET molecules in **2** viewed down the *a* axis. Carbon, grey; sulfur, yellow; hydrogen, white.

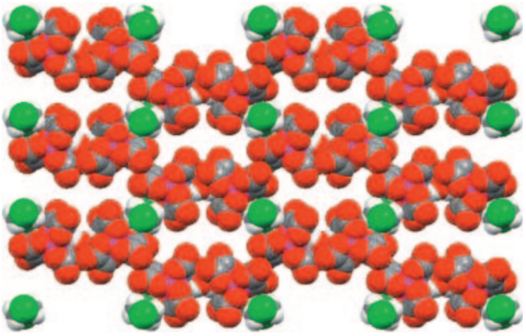

Figure 5. The anion layer in **2** viewed down the *a* axis. Carbon, grey; oxygen, red; germanium, pink; chlorine, green; hydrogen, white.

twisted conformations at both ends which are eclipsed. There are no short face-to-face S···S close contacts within stacks but there are several between adjacent stacks (S10···S23 3.51(1) Å, S11···S16 3.55(1) Å, S11···S24 3.55(1) Å, S12···S23 3.56(1) Å, S15···S18 3.42(1) Å, S15···S20 3.48(1) Å, S2···S26 3.37(1) Å, S4···S23 3.54(1) Å, S3···S24 3.58(1) Å, S9···S24 3.42(1) Å, S8···S25 3.57(1) Å, S7···S26 3.51(1) Å, S4···S26 3.56(1) Å, S8···S27 3.47(1) Å, and S7···S28 3.52(1) Å).

The anion layer is shown in Figure 5. Similar to other salts in the series of BEDT-TTF salts with tris(oxalato)metallate we observe a 50:50 distribution of the Δ and Λ enantiomers of the anion. The tris(oxalato)germanate anions are arranged in columns in the *b* direction with each column consisting of only a single enantiomer of either Δ- or Λ-$[Ge(C_2O_4)_3]^{2-}$. Columns are segregated by dichloromethane molecules, and adjacent columns consist of the opposite chirality of $[Ge(C_2O_4)_3]^{2-}$ leading to an overall achiral lattice. Within a column the tris(oxalato)germanate anions form adjacent pairs of the same enantiomer with one rotated at an angle of 90 degrees to the other. The dichloromethane molecule sites in a cavity between tris(oxalato)germanate anions and is disordered over two sites. We found a Fourier peak in another cavity (Figure 5) which we assigned to H_2O and refined. The occupancy was found to be 0.09.

In BEDT-TTF salts **1** and **2** the use of $[Ge(C_2O_4)_3]^{2-}$ leads to anion layers which differ greatly from those found when using $[M(C_2O_4)_3]^{3-}$ (M = Fe, Cr, Ga, Al, and Co). The anion layers in the salts of the type $(BEDT\text{-}TTF)_4[(A)M^{3+}(C_2O_4)_3]\cdot$solvent all have a hexagonal packing arrangement containing a solvent molecule within the hexagonal cavity. This anion packing arrangement leads to a superconducting β'' packing arrangement of BEDT-TTF when a variety of solvents are used. The shape of the $[Ge(C_2O_4)_3]^{2-}$ anion is the same as that of the M^{3+} trisoxalates, having D_3 symmetry. The $[Ge(C_2O_4)_3]^{2-}$ anion is slightly smaller in size than $[Ga(C_2O_4)_3]^{3-}$ or $[Cr(C_2O_4)_3]^{3-}$ found in related nitrobenzene salts.[6] At 298 K in **2** Ge–O bond lengths are in the range 1.83(1)–1.93(1) Å compared to Ga–O 1.98(1)–2.00(1) Å and Cr–O 1.96(1)–1.98(1) Å. The C–C bond lengths are also shorter in **2**, Ge–O 1.51(1)–1.53(1) Å versus Ga–O 1.53(1)–1.54(1) Å and Cr–O 1.57(1) Å. C–O lengths are comparable in Ge, Ga and Cr trisoxalates C=O 1.19(1)–1.23(1) Å, C–O 1.28(1)–1.35(1) Å. This small change in size and shape of the anion is unlikely to be responsible for the drastic changes observed in the BEDT-TTF packing modes hence we conclude that the change from M^{3+} to M^{4+} is responsible for dictating the packing mode of the donor.

Physical Measurements. Raman Spectroscopy: The asymmetric unit of **1** contains two and a half crystallographically independent BEDT-TTF molecules and one tris(oxalato)germanate molecule. The formula of $(BEDT\text{-}TTF)_5[Ge(C_2O_4)_3]_2$ suggests that a charge of 4+ is shared between the five BEDT-TTF molecules.

Raman spectroscopy can provide an indication of the charges on BEDT-TTF molecules by studying the two symmetric Raman active C=C stretching frequencies between 1400 and 1550 cm^{-1} (ν_3 and ν_4).[21] The spectrum for **1** shows a very strong peak at 1405 cm^{-1} and a slightly weaker peak at 1461 cm^{-1}, which shows the presence of BEDT-TTF^{1+}. The spectrum also gave smaller peaks at 1510 and 1550 cm^{-1} suggesting the presence of BEDT-TTF^0. This shows agreement with the bond length analysis for **1** which suggests that the stucture consists of dimers of BEDT-TTF^{1+} (central C=C of A and B 1.403 and 1.399 Å) and monomers of BEDT-TTF^0 (central C=C of C 1.357 Å).

The asymmetric unit of **2** contains three and a half crystallographically independent BEDT-TTF molecules. The formula of $(BEDT\text{-}TTF)_7[(Ge(C_2O_4)_3]_2\cdot 0.87CH_2Cl_2\cdot 0.09H_2O$ suggests that a charge of 4+ is shared between seven BEDT-TTF molecules. The Raman spectra collected for crystals of **2** show a single very broad peak ν_4 peak ranging from 1430 to 1460 cm^{-1} which suggests that the BEDT-TTF molecules have charges in the range 0.5+ to 0.8+.

Electrical Resistivity: Reproducible four-probe resistivity measurements were measured along the *b* axis for **1** and in the *bc* conducting plane for **2**. Both are semiconductors exhibiting simple Arrhenius behavior. The room temperature resistivity of **1** is 1010 Ω cm and activation energy calculated as 0.225 eV (Figure 6). The room temperature resistivity of **2** is 0.572 Ω cm with an activation energy of 0.172 eV between 293 and 150 K. Below 140 K the activation energy is 0.117 eV (Figure 7). Salt **1** has no 1-, 2-, or 3-dimensional conducting packing directions, on the other hand, salt **2** has an α-like 2-dimensional conducting sheet. Therefore, the resistivity of **1** is significantly higher than that of **2**. Band structure calculation was performed for **2** (Figure S1).[22] Overlap integrals indicate that the BEDT-TTF stacks have a dimer–trimer–dimer arrangement. Similar to

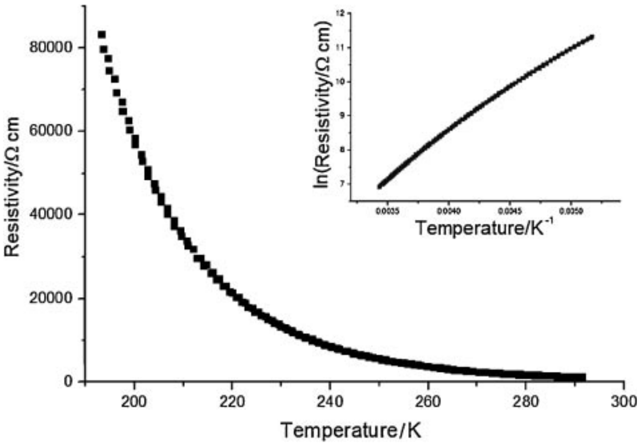

Figure 6. Temperature variation of four probe DC resistance for **1**. Inset: plot of $\ln(R/\Omega\,\mathrm{cm})$ vs. $1/T$.

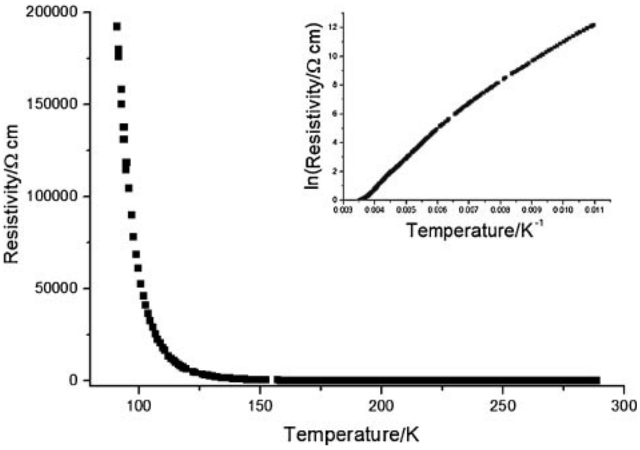

Figure 7. Temperature variation of four probe DC resistance for **2**. Inset: plot of $\ln(R/\Omega\,\mathrm{cm})$ vs. $1/T$.

other α-type BEDT-TTF salts, **2** has a Fermi surface but the salt shows only semiconducting behavior.

Conclusion

Two new BEDT-TTF–tris(oxalato)germanate salts have been synthesized and characterized. These salts represent new examples of both cation and anion layer packing in the series of BEDT-TTF salts containing tris(oxalato)metallate anions.

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Supporting Information

Figure S1 is band calculation results for **2**. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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