

Communication

Solvent-Included Ternary Charge-Transfer Salt (BEDT-TTF)₂GaCl₄(C₆H₅Cl)_{0.5}, (BEDT-TTF = Bis(ethylenedithio)-tetrathiafulvalene)

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Abstract: The synthesis, crystal structure, and conductivity of a solvent-included ternary charge-transfer salt (BEDT-TTF)₂GaCl₄(C₆H₅Cl)_{0.5} (**1**) is described and interpreted. Electrochemical oxidation of neutral bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF) in the presence of (Me₄N)Ga(C₂O₄)Cl₂ in a mixture of C₆H₅Cl and C₂H₅OH yields crystals of **1**. Compound **1** crystallized as a monoclinic *C* 2/*c* space group with cell parameters: $a = 47.0615(4)$ Å, $b = 6.7895(1)$ Å, $c = 31.6297(4)$ Å, $\beta = 132.064(1)^\circ$, $V = 7503.0(2)$ Å³, $Z = 8$ at 293 K and $a = 46.4767(5)$ Å, $b = 6.7398(1)$ Å, $c = 31.0778(4)$ Å, $\beta = 131.630(1)^\circ$, $V = 7267.4(2)$ Å³, $Z = 8$ at 120 K. The formal charge of the donor molecule was assigned as +0.5 from bond lengths in the TTF core. The donor molecules stack with C—⋯S contacts along the *c* direction and side-to-side S⋯S contacts along the *b* direction to form a two-dimensional donor layer on the *bc* plane. In the anion sheet, C₆H₅Cl chain is sandwiched by two GaCl₄[−] chains with Cl⋯Cl contacts. Compound **1** shows semiconductive behavior with $E_\alpha = 124$ meV between room-temperature and 150 K and $\sigma_{300K} = 1$ S·cm^{−1}.

Keywords: organic conductor; solvent molecule; crystal structure; charge-transfer salt

1. Introduction

In a charge-transfer salt, the conductivity is usually controlled by the arrangement of the conducting π -unit, such as TTF (TTF = tetrathiafulvalene), BEDT-TTF, $M(\text{dmit})_2^{n-}$ (dmit = 1,3-dithiole-2-thione-4,5-dithiolate), and their derivatives [1]. Recently, it has been found that the conductivity can be influenced by the solvent molecules which exist in the counterion layer [2]. Depending on the crystal structure of the reported binary charge-transfer salts, interesting physical properties of the ternary charge-transfer salts are expected. So the synthesis and characterization of the binary and ternary compounds is necessary in order to achieve a deep understanding of the molecular conductor. The binary charge-transfer salt of GaCl_4^- has been reported [3,4]. Because FeCl_4^- and GaCl_4^- could be replaced arbitrarily, the charge-transfer salt of GaCl_4^- is an important reference for a molecule-based magnetic conductor [3,4]. A ternary charge-transfer salt of BEDT-TTF, GaCl_4^- and solvent molecule $\text{C}_6\text{H}_5\text{Cl}$ was obtained when looking for the charge-transfer salt of [BEDT-TTF] and $[\text{Ga}(\text{C}_2\text{O}_4)\text{Cl}_2^-]$. Its crystal structure and conductivity are reported here.

2. Results and Discussion

During the process of electrochemical oxidation of BEDT-TTF in a mixture of $\text{C}_6\text{H}_5\text{Cl}$ and $\text{C}_2\text{H}_5\text{OH}$, the electrolyte $(\text{CH}_3)_4\text{NGa}(\text{C}_2\text{O}_4)\text{Cl}_2$ decomposed into $\text{Ga}(\text{C}_2\text{O}_4)_3^{3-}$ and GaCl_4^- . $\text{Ga}(\text{C}_2\text{O}_4)_3^{3-}$ was transferred into GaCl_4^- when chlorinated alkane existing as κ' -BETS $_2\text{FeCl}_4$ was obtained from BETS, $((\text{CH}_3)_4\text{N})_3\text{Fe}(\text{C}_2\text{O}_4)_3$ in $\text{C}_6\text{H}_5\text{Cl}$ [5]. The ternary charge-transfer salt **1** is composed of BEDT-TTF, GaCl_4^- and $\text{C}_6\text{H}_5\text{Cl}$. We failed to obtain a high quality single crystal of **1** when $(\text{CH}_3)_4\text{NGaCl}_4$ was used as electrolyte.

There are two BEDT-TTF molecules (A, B), one GaCl_4^- and half a molecule of $\text{C}_6\text{H}_5\text{Cl}$ in an independent unit of **1** as shown Figure 1. The Cl on the solvent molecule is disordered in two positions, and C7 is disordered in two positions at 293 K and 120 K. The formal charge of the BEDT-TTF molecule assigned from bond lengths on TTF cores (Table 2) is +0.5 as in Table 2 [6].

Except for the ethylene groups, all of the atoms on the two BEDT-TTF molecules (A, B) are coplanar with separate deviations of 0.08 and 0.08 Å. The packing is generated by the symmetry operation with the $C 2/c$ space group as shown in Figure 2. BEDT-TTF molecules stack in the sequence of $\cdots\text{AABBAABB}\cdots$ with the main planes parallel to each other to form a column along the c axis. There are intermolecular C \cdots S contacts through hydrogen bonds between AA, AB and BB along the c -axis, S \cdots S contacts between AA, BB along the b -axis and between AB along the c -axis in a donor-layer as in Figure 3.

In the anion sheet, the $\text{C}_6\text{H}_5\text{Cl}$ chain is sandwiched by two GaCl_4^- chains along the b axis, and the shortest Cl \cdots Cl distance is 3.592 Å between $\text{C}_6\text{H}_5\text{Cl}$ and GaCl_4^- , 3.813 Å between two GaCl_4^- anions as shown in Figure 4. Ga \cdots Ga distances are 6.790 Å along the b axis, 9.368 Å between two GaCl_4^- chains intercalated by a $\text{C}_6\text{H}_5\text{Cl}$ chain, and 7.306 Å between neighboring GaCl_4^- chains. There are short contacts between donor and anion: S \cdots Cl (S7 \cdots Cl1 3.554(1) Å, S6 \cdots Cl3 3.572(1)) Å, C–H \cdots Cl (C7A–H7A \cdots Cl3 2.86 Å/159.3°, C7B–H7BB \cdots Cl3 2.83 Å /170.2°, C17–H17A \cdots Cl3 2.94 Å /174.6°), and between donor and solvent molecule C18–H18B \cdots Cl5 2.90 Å/124.1°. Compound **1** crystallized as monoclinic with cell parameters: $a = 47.0615(4)$ Å, $b = 6.7895(1)$ Å, $c = 31.6297(4)$ Å, $\beta = 132.064(1)^\circ$, $V = 7503.0(2)$ Å 3 , $Z = 8$ at 293 K, space group $C 2/c$. It remained the same until

120 K. The binary compound (BEDT-TTF)₂GaCl₄ (**2**) crystallized as triclinic with cell parameters: $a = 31.911(6)$ Å, $b = 16.580(4)$ Å, $c = 6.645(2)$ Å, $\alpha = 98.15(2)^\circ$, $\beta = 85.60(2)^\circ$, $\gamma = 90.55(2)^\circ$, $V = 3470$ Å³, $Z = 4$ at 298 K, space group $P\bar{1}$ [3]. In **2**, a donor layer was formed on the bc plane with BEDT-TTF packed face-to-face along the b axis and side-by-side along the c axis, the S...S contact was observed between donor molecules along the b axis as dimerization. The donor layer and the anion layer were stacked alternatively along the a axis in **1** and **2**. The tilted angle of the donor molecule to the anion layer is 80° in **1** and 70° in **2**, so the a axis expanded from 31.911 Å in **2** to 47.062 Å in **1**. The unit cell parameters of **1** are related to **2** by the transfer matrix (1,0,0; 0,0,-1; 0,1,0). From **2** to **1**, the b axis is doubled, α and β angles are shifted to 90° , and are accompanied by a space group change from $P\bar{1}$ to $C2/c$. The main difference between **1** and **2** is the dimerization of the donor in **2**, which does not exist in **1**.

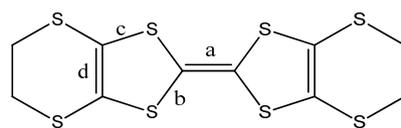
Table 1. Crystallographic data of **1**.

Compound	1	1
formula	C23H18Cl4.50GaS16	C23H18Cl4.50GaS16
Fw	1036.58	1036.58
F(000)	4156	4156
T , K	120	293
crystal system	monoclinic	monoclinic
space group	$C2/c$	$C2/c$
a , Å	46.4767(5)	47.0615(4)
b , Å	6.7398(1)	6.7895(1)
c , Å	31.0778(4)	31.6297(4)
α , °	90	90
β , °	131.630(1)	132.064(1)
γ , °	90	90
V , Å ³	7276.4(2)	7502.99(16)
Z	8	8
D_c , g/cm ³	1.892	1.835
μ (Mo $K\alpha$), mm ⁻¹	2.027	1.966
crystal size, mm ³	$0.34 \times 0.24 \times 0.10$	$0.34 \times 0.24 \times 0.10$
T_{\min} and T_{\max}	0.417, 0.916	0.556, 0.839
θ_{\min} , θ_{\max} , °	0.994, 27.50	0.993, 27.54
no. total reflns.	55220	58492
no. uniq. reflns (R_{int})	8324(0.0863)	8587(0.0843)
no. obs. [$I \geq 2\sigma(I_0)$]	5590	4933
no. params	425	425
$R1, wR2$ [$I \geq 2\sigma(I_0)$]	0.0370, 0.0797	0.0392, 0.0918
$R1, wR2$ (all data)	0.0723, 0.0877	0.0911, 0.1042
GOF	0.967	0.974
^a $\Delta\rho$, e/Å ³	0.773/−0.874	0.559/−0.501
^b Max. and mean Δ/σ	0.001/0.000	0.001/0.000
CCDC	794827	794828

The temperature dependent resistance of **1** is shown in Figure 5. It showed semiconductive behavior from 300 K to 150 K with $E_\alpha = 0.124$ eV and $\sigma_{\text{rt}} = 1$ S cm⁻¹ for **1**, 150 K to 110 K with $E_\alpha = 0.041$ eV. The conductivity is higher than δ -(BEDT-TTF)₂GaCl₄ with $\sigma_{\text{rt}} = 0.1$ S cm⁻¹, $E_\alpha = 0.2$ eV as expected from the donor arrangement as no dimerization was observed [3]. The conductivity is lower than the

bilayered magnetic charge-transfer salt δ -(BEDT-TTF)₃(FeCl₄)₂ because the conductivity in δ -(BEDT-TTF)₃(FeCl₄)₂ is contributed to from both layer-A and layer-B with an anisotropic room-temperature conductivity range from 4.6~120 S·cm⁻¹ [7]. This corresponds with the expectancy that the conductivity of the charge-transfers salts is dominated by the arrangement of the BEDT-TTF molecules. The dimerization of the donor disappears when the solvent molecule is included and the conductivity of the crystal increases.

Table 2. Bond lengths of the tetrathiafulvalene (TTF) core.



$$\delta = (b + c) - (a + d)$$

$$Q = 6.437 - 7.463\delta$$

Donor	a	b	c	d	δ	Q	
120 K							
ET1	1.363(4)	1.735(3)	1.744(3)			0.77575	0.65
		1.736(3)	1.744(3)	1.353(4)			
		1.737(3)	1.746(3)	1.335(4)			
		1.738(3)	1.751(3)				
ET2	1.363(4)	1.739(3)	1.745(3)			0.77325	0.67
		1.737(3)	1.745(3)	1.338(4)			
		1.739(3)	1.742(3)	1.354(4)			
		1.736(3)	1.746(3)				
290 K							
ET1	1.365(4)	1.730(4)	1.741(3)			0.7665	0.72
		1.734(3)	1.739(3)	1.353(4)			
		1.732(3)	1.746(3)	1.336(4)			
		1.734(3)	1.748(3)				
ET2	1.357(4)	1.744(3)	1.744(3)			0.786	0.57
		1.739(3)	1.746(3)	1.337(4)			
		1.733(3)	1.746(3)	1.344(4)			
		1.741(3)	1.741(4)				

Figure 1. Oak Ridge Thermal Ellipsoid Plot (ORTEP) drawing of **1** with 30% ellipsoid at 120 K.

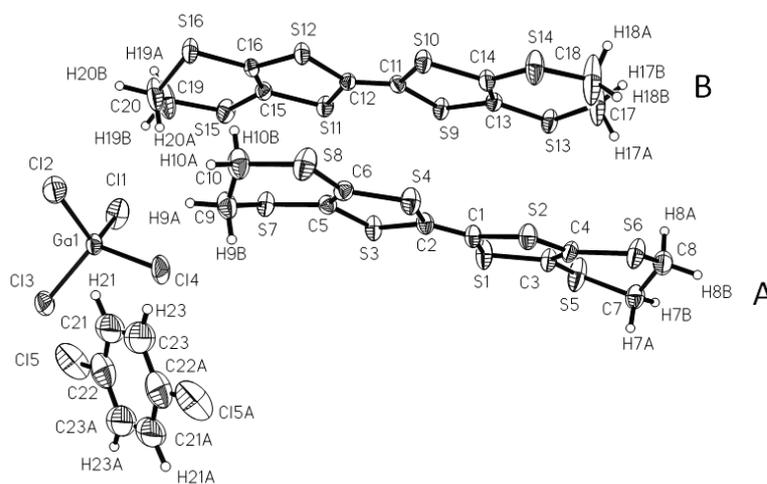


Figure 2. Packing diagram of **1** along the *b* axis at 120 K. H and disordered atoms on the donor were omitted for clarity. Dashed lines are C–H⋯Cl, Cl⋯Cl contacts.

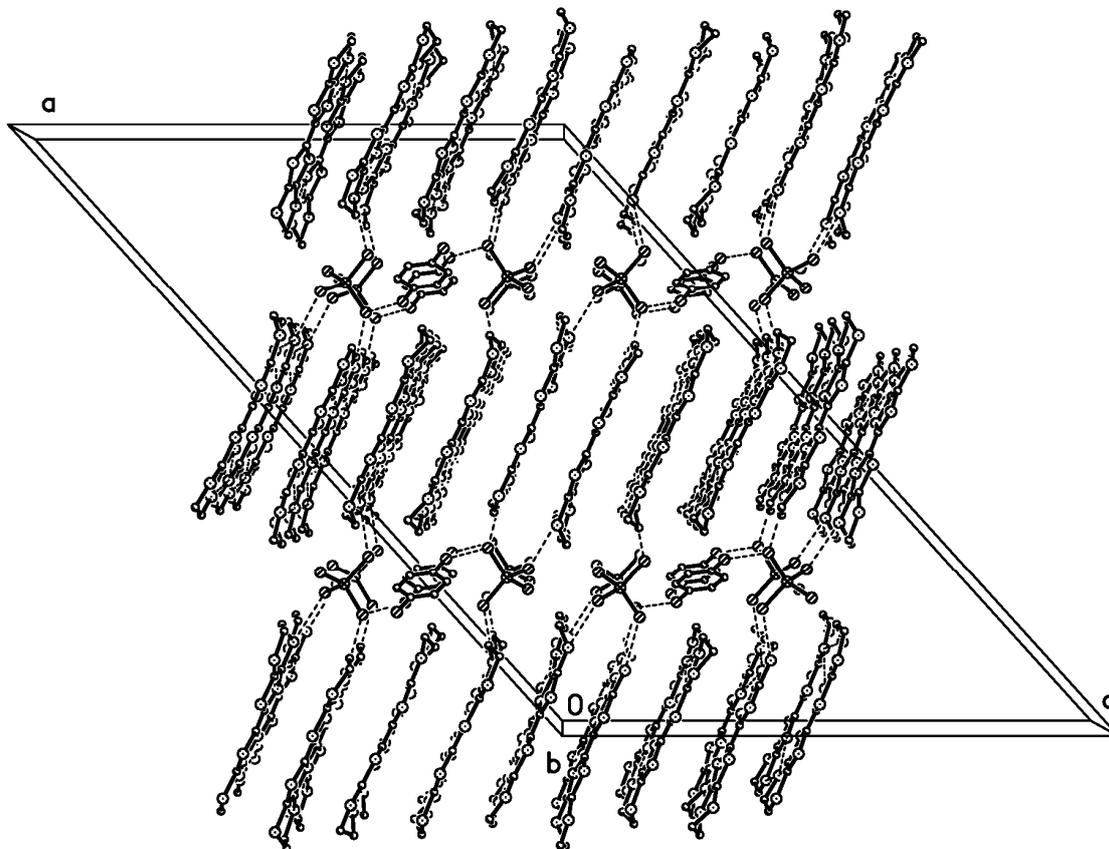


Figure 3. Donor arrangement on the *bc* plane. H and disordered atoms were omitted for clarity.

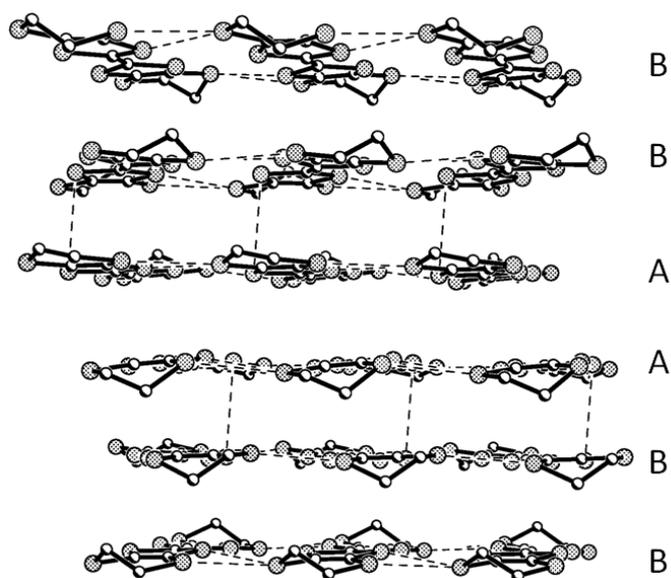


Figure 4. GaCl_4^- and $\text{C}_6\text{H}_5\text{Cl}$ in the anion layer. Dashed lines are $\text{Cl}\cdots\text{Cl}$ contacts between anion and solvent.

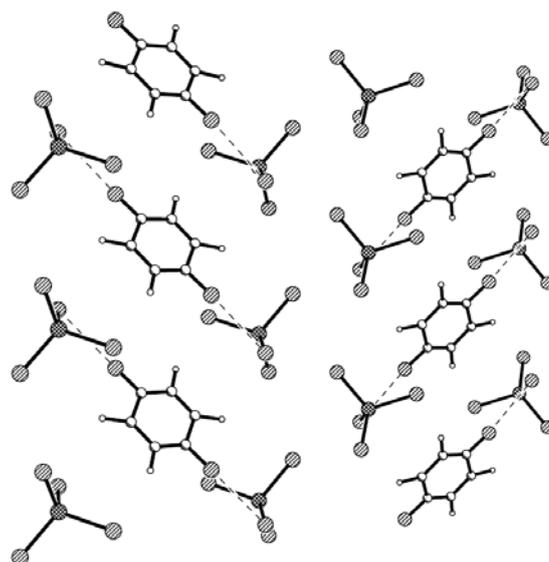
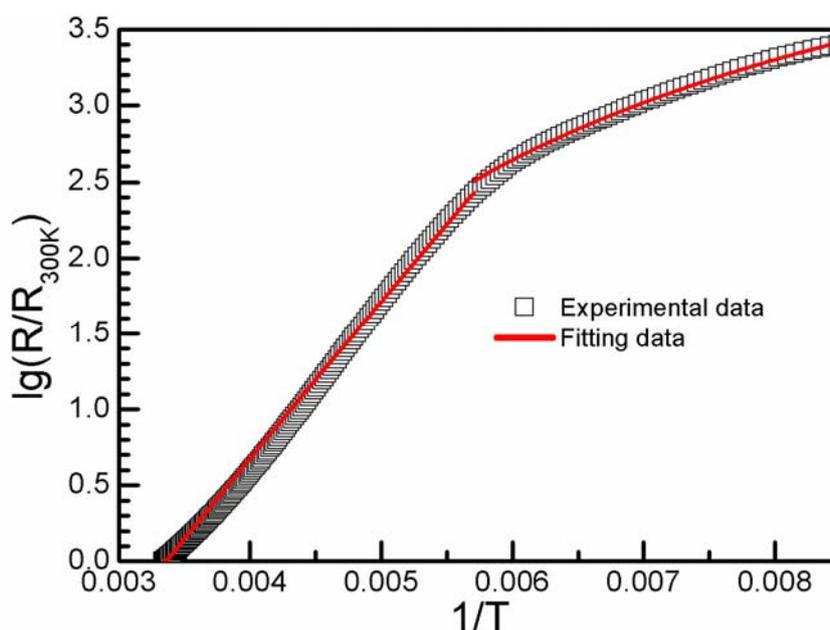


Figure 5. Temperature-dependent resistivity of **1**.



3. Experimental Section

All reagents are commercially available and were used as received without further purification unless otherwise stated. Block colorless crystalline $(\text{CH}_3)_4\text{NGa}(\text{C}_2\text{O}_4)\text{Cl}_2$ was synthesized from 1 mmol $[(\text{CH}_3)_4\text{N}]_3\text{Ga}(\text{C}_2\text{O}_4)_3$ and 2 mmol GaCl_3 in 10 mL H_2O . The products were recrystallized twice from ethanol. $(\text{CH}_3)_4\text{NFe}(\text{C}_2\text{O}_4)\text{Cl}_2$ is isostructural as reported [8]. $\text{C}_6\text{H}_5\text{Cl}$ and $\text{C}_2\text{H}_5\text{OH}$ were distilled before use.

5.0 mg BEDT-TTF, 15.0 mg $(\text{CH}_3)_4\text{NGa}(\text{C}_2\text{O}_4)\text{Cl}_2$ were dissolved in a mixture of 25.0 mL $\text{C}_6\text{H}_5\text{Cl}$ and 5.0 mL $\text{C}_2\text{H}_5\text{OH}$. The platelike dark brown single crystal of $(\text{BEDT-TTF})_4(\text{GaCl}_4)_2\cdot\text{C}_6\text{H}_5\text{Cl}$ (**1**) was obtained by an electrocrystallization method with a Pt cathode at 0.20 μA for two weeks.

X-ray diffraction data of **1** were collected on a Nonius Kappa CCD diffractometer with graphite monochromated Mo $\text{K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation at 290 K and 120 K. Lorentz, polarization, and empirical absorption corrections were carried out [9]. The crystal structure was solved by the direct method and refined by full-matrix least-squares on F^2 using the SHELX program, with anisotropic thermal parameters for all non-hydrogen atoms [10]. The hydrogen atoms on the ethyl groups were determined by calculation. Crystallographic data and refinement parameters are summarized in Table 1. Two sets of structure data have been deposited at the Cambridge Crystallographic Data Centre.

The measurement of the resistance as a function of the temperature from 300 K to 2 K was carried out on a Quantum Design PPMS 9 system by a four-probe method. Twenty μm Au wires were attached to a single crystal by gold paste on the best developed surface.

4. Conclusions

When a solvent molecule was included in a binary charge-transfer salt $(\text{BEDT-TTF})_2\text{GaCl}_4$, the dimerization of the donor molecules disappeared, and the conductivity increased in the ternary charge-transfer salt $(\text{BEDT-TTF})_2\text{GaCl}_4(\text{C}_6\text{H}_5\text{Cl})_{0.5}$. New magnetic conductors can be expected when solvent molecules are intercalated into binary charge-transfer salts of FeCl_4^- [7].

Acknowledgments

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