Preparation, Crystal and Electronic Structures, and Electrical Resistivity of $(BEDT\text{-}TTF)_3Cl_{2.5}(H_5O_2)$

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The crystal and electronic structures and electrical resistivity of new chlorine complex, (BEDT-TTF)$_3$Cl$_{2.5}$(H$_5$O$_2$), were investigated. The two-dimensional donor sheet and the anion layer stack alternately along the *b*-axis. The packing pattern of donors is similar to that of (BEDT-TTF)$_3$(ClO$_4$)$_2$ and the sharp metal-insulator transition was observed at 170 K. It is interesting that not only donor and anion but also the third component cation, H^+, determines the 3/4-filled band structure.

In the past several years, a number of BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) complexes have been prepared and a variety of structural and physical properties have been investigated. Recently we have searched for new conductors based on BEDT-TTF including metal pseudohalide anions (cyanometalate or thiocyanatometalate anion) which form an anion cluster or a polymer. On the course of this study, we have found four organic superconductors, κ-(BEDT-TTF)$_2$Cu(NCS)$_2$,[1a] κ-(BEDT-TTF)$_2$Ag(CN)$_2$H$_2$O,[1b] (BEDT-TTF)$_4$Pt(CN)$_4$H$_2$O,[1c] and (BEDT-TTF)$_4$Pd(CN)$_4$H$_2$O.[1d]

In the present work, we study the new Cl^- complex which was eventually obtained on preparing the Hg(CN)$_2$ salt; the Cl^- anion may come from the solvent of 1,1,2-trichloroethane. So far three chlorine complexes have been prepared, (BEDT-TTF)$_4$Cl$_2$(H$_2$O)$_4$,[2a] (BEDT-TTF)$_4$Cl$_2$(H$_2$O)$_6$,[2b] and (BEDT-TTF)$_3$Cl$_2$(H$_2$O)$_2$,[2c] and two of three salts were happened to be obtained by using an electrolyte or a solvent including chlorine. Only the last one can be a superconductor at 2 K under 16 kbar.[2c] The present communication reports the crystal and electronic structures and electrical resistivity of the forth chlorine complex, (BEDT-TTF)$_3$Cl$_{2.5}$(H$_5$O$_2$).

Experimental

The black plate crystals were obtained by electrochemical oxidation of BEDT-TTF in the presence of Hg(CN)$_2$, KCN, 18-crown-6 ether in 1,1,2-trichroloethane and 10% vol. ethanol after 9 months. The anion Cl^- instead of $[Hg(CN)_4]^{2-}$ was derived from the solvent of 1,1,2-trichloroethane.

Crystal Data: $C_{30}H_{29}O_2S_{24}Cl_{2.5}$ F.W.=1279.75, triclinic, space group $P\bar{1}$, a=10.235(2), b=15.466(3), c=7.643(1) Å, α=98.28(2)°, β=98.01(2)°, γ=86.11(1)°, V=1184.1(4) Å^3, Z=1, and D_c=1.081 g cm^{-1}. After the observation of the presence of S and Cl atoms and the absence of Hg atom by EPMA, the crystal structure was solved by the direct method (SHELXS86[3]) and the succeeding Fourier syntheses and refined by using 2782 independent reflections (Mo $K\alpha$, $2\theta<60°$, $|F_o|>3\sigma(|F_o|)$) to an R value of 0.041. Thermal parameters were anisotropic for all non-hydrogen atoms and isotropic for hydrogen atoms.

The electrical resistivity was measured by the 4-probe method with the gold paint as the contacts.

Results and Discussion

The atomic coordinates are listed in Table 1 and the molecular structures of BEDT-TTF are depicted in Fig. 1. Figure 2 shows the crystal structures of (BEDT-TTF)$_3$Cl$_{2.5}$(H$_5$O$_2$). One BEDT-TTF molecule is present on the general position and the other is on the inversion center. The donor sheet is sandwiched by the anion layer along the *b*-axis. Some close contacts between donor and anion layers are observed as shown by dotted lines in Fig. 2. The contacts indicated by Cl···H(donor) and O(1)···H(donor) are less than 3.12 and 2.72 Å, respectively.

The donor arrangement is depicted in Fig. 3. The packing pattern of donors is close to (BEDT-TTF)$_3$(ClO$_4$)$_2$:[4] The trimer stacks not only in the [101], but also [10$\bar{1}$] and [20$\bar{1}$] directions. The salts of ClO_4-type usually afford the uniform charge as $(donor)^{2/3+}$ due to the 3(donor):2(anion) stoichiometry. However, in this salt, (BEDT-TTF)$_3$Cl$_{2.5}$(H$_5$O$_2$), the charge of three donors is +0.5 since the anion layer contains $[Cl_{2.5}(H_5O_2)]^{-1.5}$. The distances of central C=C

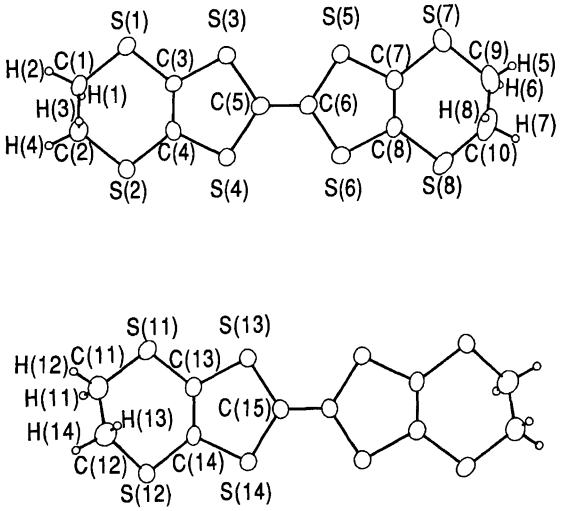

Fig. 1. Molecular structures of BEDT-TTF.

Table 1. Atomic Parameters ($\times 10^4$) of $(BEDT\text{-}TTF)_3Cl_{2.5}(H_5O_2)$

Atom	x	y	z	B_{eq}
Cl(1)	5000	5000	5000	3.98
Cl(2)	1186	5373	9369	4.93
O(50)	3979	4745	8634	5.43
H(50)	4275	4868	7619	5.89
H(51)	3185	4945	8810	7.93
H(52)	5000	5000	10000	9.38
S(1)	4808	−1719	3263	3.35
S(2)	1843	−2484	787	3.08
S(3)	3211	−109	4122	2.84
S(4)	760	−726	2017	2.84
S(5)	1734	1760	5234	2.90
S(6)	−715	1147	3156	2.93
S(7)	707	3540	6361	3.58
S(8)	− 2279	2785	3949	3.47
S(11)	1454	2240	137	4.37
S(12)	4250	2962	2991	2.87
S(13)	3035	614	−578	2.68
S(14)	5398	1200	1811	2.75
C(1)	4387	−2841	2485	3.33
C(2)	3509	−2955	701	3.27
C(3)	3260	−1167	3008	2.27
C(4)	2128	−1458	2018	2.44
C(5)	1548	118	3421	2.19
C(6)	928	913	3890	2.35
C(7)	376	2504	5200	2.42
C(8)	−758	2213	4246	2.26
C(9)	−874	4097	6051	8.51
C(10)	−1803	3865	4615	8.41
C(11)	1662	3290	1362	5.02
C(12)	3021	3610	1743	4.58
C(13)	2931	1666	623	2.63
C(14)	4040	1942	1721	2.09
C(15)	4663	383	268	2.26
H(1)	3864	−3091	3367	7.56
H(2)	5146	−3206	2414	5.21
H(3)	3966	−2688	−124	6.63
H(4)	3505	−3546	274	5.48
H(5)	−769	4625	6117	6.37
H(6)	−1356	4024	6973	9.60
H(7)	−2540	4220	4792	6.29
H(8)	−1375	4074	3723	7.89
H(11)	1420	3362	2437	7.53
H(12)	1072	3704	800	5.88
H(13)	3235	3612	561	9.18
H(14)	2982	4193	2339	4.11

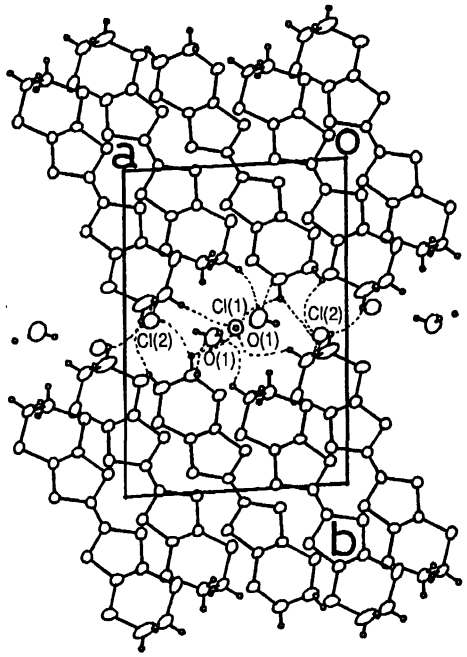

Fig. 2. Crystal structure of $(BEDT\text{-}TTF)_3Cl_{2.5}(H_5O_2)$.

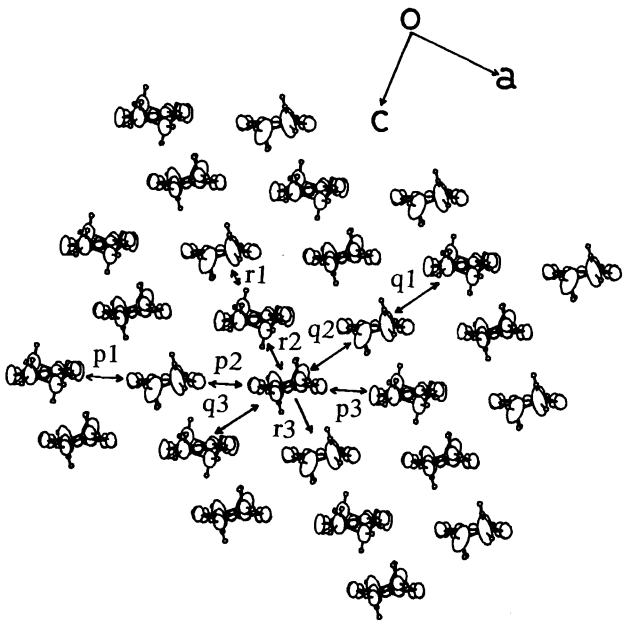

Fig. 3. Donor arrangement of $(BEDT\text{-}TTF)_3Cl_{2.5}(H_5O_2)$.

bond in two crystallographically independent BEDT-TTF molecules, 1.369(7) and 1.370(7) Å, are close to that of $(BEDT\text{-}TTF)^{+0.5}$ (Table 2 and Fig. 1).[5]

The anion arrangement is shown in Fig. 4. The Cl^- (1) anion on the inversion center is connected to two H_2O molecules through hydrogen bonds. Since the measurement of EPMA clarifies that this salt contains only Cl and S atoms larger than Na atom, the presence of Cl(2) is evident and the occupation possibility of Cl(2), 0.75, is refined by the least-square procedure. There is no possibility that the O atom is present at the position of Cl(2) because the temperature factor of the O atom is calculated to be B_{eq}=0.95 and the final R value, 0.055, is much higher when the O atom is allocated instead of Cl(2). The distance between O(1) and O(1)′ atom of H_2O molecules, 2.808(7) Å, is close each other. Therefore the H^+ cation on an inversion center is related to two O atoms like $[H_2O\cdots H^+\cdots OH_2]$ due to the ionic stability. As the result unique one-dimensional anion polymer, $[\cdots O\text{–}H\cdots\cdots Cl^-\cdots\cdots H\text{–}O\cdots\cdots H^+\cdots\cdots O\text{–}H]_n$, $(Cl^-)_{0.75}\cdots H$ $(Cl^-)_{0.75}\cdots H$ $(Cl^-)_{0.75}\cdots H$ is extended along the c-axis. Thus one anion unit

Table 2. Bond Lengths (Å) of the TTF Skeleton of BEDT-TTF and the Average with the mmm Symmetry

	A	B	$D^{+1/2}$
C5–C6	1.369(7)	1.370(7)	1.365
C5–S3	1.740(5)	1.734(5)	1.740
C5–S4	1.733(5)	1.734(5)	
C6–S5	1.724(5)		
C6–S6	1.727(5)		
Average	1.731	1.734	
C3–S3	1.733(5)	1.754(5)	1.763
C4–S4	1.740(5)	1.742(5)	
C7–S5	1.743(5)		
C8–S6	1.738(5)		
Average	1.738	1.748	
C3–C4	1.358(7)	1.368(7)	1.329
C7–C8	1.350(7)		
Average	1.354	1.368	

$D^{+1/2}$: α-(BEDT-TTF)$_2$PF$_6$.

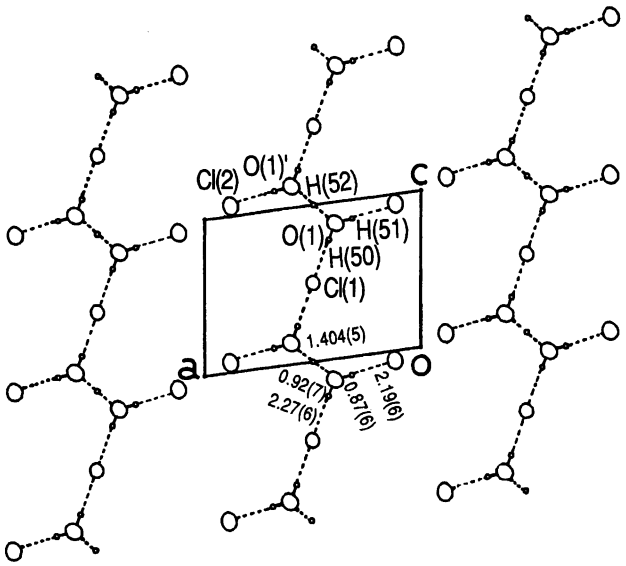

Fig. 4. Anion arrangement of (BEDT-TTF)$_3$Cl$_{2.5}$(H$_5$O$_2$) projected along the b^*-axis.

[Cl$_{2.5}$(H$_5$O$_2$)] has a charge −1.5, which is consistent with the charge on the BEDT-TTF molecules, BEDT-TTF$^{+0.5}$.

Two similar examples where a H atom or cation is sandwiched by two close O atoms follow. In (BEDT-TTF)$_3$Cl$_2$(H$_2$O)$_2$,[6] the anion layer is composed of [Cl$_4$(H$_2$O)$_4$] unit, where the H atoms of H$_2$O molecule is sandwiched by two O atoms which is apart by 2.789(7) Å like [(Cl$^-$)···H–O–H···O–H···Cl$^-$···H–O···H–O–H···(Cl$^-$)]. The other example is (BT)$_2$Cl$_2$(H$_5$O$_2$).[7] The H$^+$ in (H$_5$O$_2$)$^+$ unit is connected with two O atoms of H$_2$O molecules by hydrogen bonds. The distance between two O atoms is 2.46 Å like [···Cl$^-$···H–O···H$^+$···O–H···Cl$^-$···]$_n$.

In order to understand the intermolecular interaction, the intermolecular overlap integrals of donor HOMO are calculated on the basis of extended Hückel method.[8] As shown in Fig. 3, the calculated overlap integrals are p1=−7.9, p2=−7.5, p3=7.8, q1=16.9, q2=14.6, q3=−16.9, r1=−1.0, r2=1.0, and r3=-4.5×10^{-3}. The integrals along the transverse [10$\bar{1}$] direction is the largest among three stacking directions, which is similar to (BEDT-TTF)$_3$(ClO$_4$)$_2$.[4] Figure 5 shows the electronic band structure calculated by the tight-binding method by using the overlap integrals. Since there are three donors in a unit cell, three energy dispersions are observed. From the stoichiometry of (BEDT-TTF)$_3$Cl$_{2.5}$(H$_5$O$_2$), the 3/4-filled band was obtained where the lower two levels are wholly and the upper level is partially occupied. The band structure is pseudo-one-dimensional though that of (BEDT-TTF)$_3$(ClO$_4$)$_2$ is semimetallic. This is due to the difference of the 2/3- and 3/4-filled band structure.

The electrical resistivity is shown in Fig. 6. The

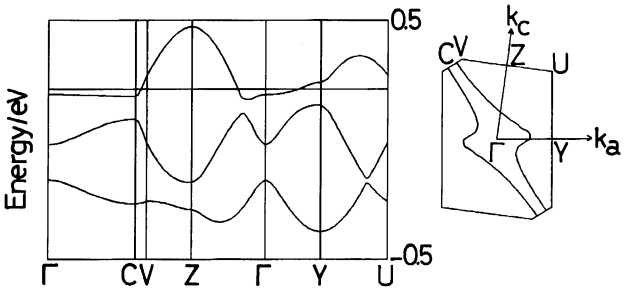

Fig. 5. Energy band structure of (BEDT-TTF)$_3$Cl$_{2.5}$(H$_5$O$_2$).

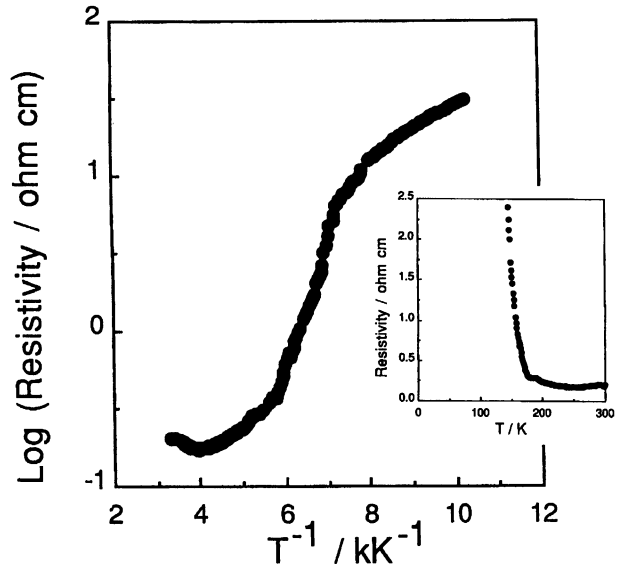

Fig. 6. Temperature dependence of electrical resistivity of (BEDT-TTF)$_3$Cl$_{2.5}$(H$_5$O$_2$).

room-temperature conductivity is 20—70 S cm^{-1}, which is ordinal value for metallic BEDT-TTF complexes. The distinct metal-insulator transition occurred around 170 K.

Last year we reported the development of conductors from two-component system like donor-acceptor, donor-anion, or cation-acceptor, to three-component system of donor-anion-cation on $(BEDT\text{-}TTF)_2MHg(SCN)_4$ (M=Li, Na, K, NH_4, Tl, Rb, and Cs).[9] Due to the variety of the third component of cation, these $MHg(SCN)_4$ salts can be a semiconductor, a metal, or a superconductor because of various packing of donors. This chlorine complex also proves that H^+ can be the third component and the cation charge has a big role to determine the band filling.

In conclusion, we have prepared the new chlorine BEDT-TTF complex, $(BEDT\text{-}TTF)_3Cl_{2.5}(H_5O_2)$, which contains not only the donor and the anion but also the third component of cation, H^+. In the anion sheet, the unique one-dimensional anion polymer is constructed like $[\cdots H^+\cdots(Cl^-)_{0.75}OH_2\cdots Cl^-\cdots H_2O\text{-}(Cl^-)_{0.75}\cdots H^+\cdots]_n$ through hydrogen bonds. The donor arrangement is similar to that of $(BEDT\text{-}TTF)_3(ClO_4)_2$ and the 3/4-filled band structure is obtained. The complex undergoes a metal-insulator transition around 170 K.

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