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THE CRYSTAL STRUCTURES OF (BEDT-TTF)ReO_4(THF)$_{0.5}$ AND (BEDT-TTF)IO_4(THF)$_{0.5}$

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The crystal structures of (BEDT-TTF)ReO_4(THF)$_{0.5}$ and (BEDT-TTF)IO_4(THF)$_{0.5}$ are reported (BEDT-TTF=bis(ethylenedithio)tetrathiafulvalene, THF=tetrahydrofuran). These salts of BEDT-TTF cations are isomorphic. There are chains of BEDT-TTF dimers. The bond lengths of BEDT-TTF$^+$ differ systematically from those of the neutral BEDT-TTF molecule.

Recently, two-dimensional(2-D) metallic properties,1) superconductivity2) and quasi-1-D conduction along the transverse direction3) were observed in BEDT-TTF complexes. Unlike the typical organic conductors such as $(TMTTF)_2X$ and $(TMTSF)_2X$ ($X=ClO_4$, PF_6, NO_3,$\cdots$), the crystals of the BEDT-TTF complexes show a variety of the crystal structures (TMTTF=tetramethyltetrathiafulvalene, TMTSF=tetramethyltetraselenafulvalene). The isomorphism of $(TMTTF)_2X$ and $(TMTSF)_2X$4) suggests a strong tendency to the face-to-face stacking of the planar donor molecules. On the other hand, in the case of BEDT-TTF, the planarity of the molecule is broken by the ethylene groups, whose steric effect prevents the infinite stacking of the BEDT-TTF molecules.

We have determined the crystal structures of neutral BEDT-TTF molecule,5) the 2:1 salts ((BEDT-TTF)$_2ClO_4(C_2H_3Cl_3)_{0.5}$,6) α-(BEDT-TTF)$_2PF_6$,7) β-(BEDT-TTF)$_2PF_6$,3) and (BEDT-TTF)$_2ClO_4(C_4H_8O_2)$8)), and the 3:2 salt ((BEDT-TTF)$_3(ClO_4)_2$).8) The side-by-side array of the molecules is a common structural feature.

In this paper, We report the crystal structures of the 1:1 salts, (BEDT-TTF)X(THF)$_{0.5}$ ($X=ReO_4$, IO_4; THF=tetrahydrofuran).

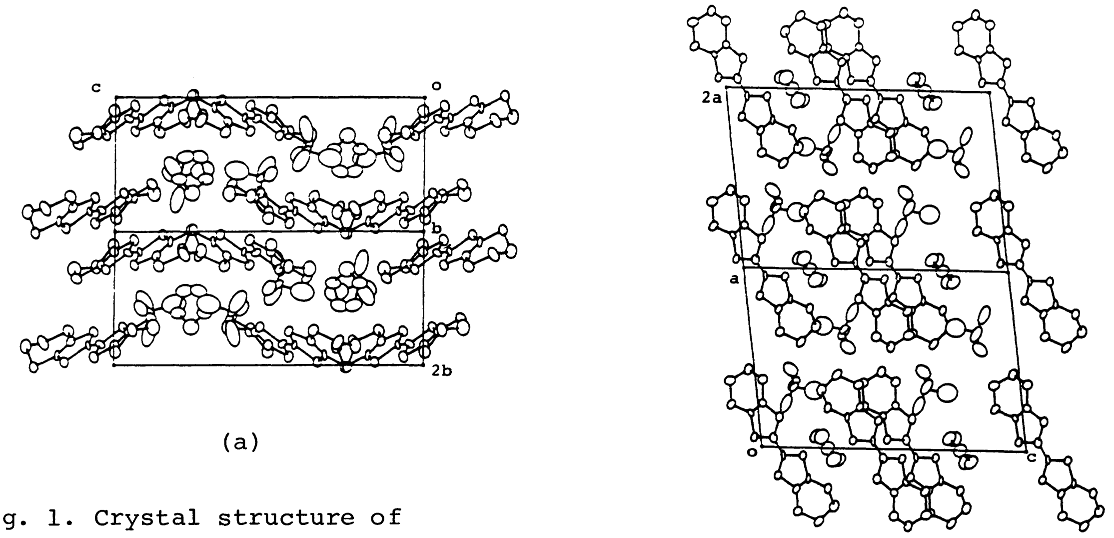
Black crystals of (BEDT-TTF)X(THF)$_{0.5}$ ($X=ReO_4$,IO_4) were grown electrochemically in THF solutions. Both the crystals are elongated plates. X-Ray crystal structure analyses have revealed that the crystals include THF molecules. Similar inclusion of the solvent molecules has been observed in the 2:1 perchlorates (1,1,2-trichloroethane[6)] and dioxane[8)]).

The crystal data are: monoclinic, P2/c, a=12.692(9), b=8.036(6), c=19.285(10) Å, β=97.66(5)°, V=1950(2) Å^3, Z=4 for (BEDT-TTF)IO_4(THF)$_{0.5}$, $(C_{10}H_8S_8)IO_4(C_4H_8O)_{0.5}$; monoclinic, P2/c, a=12.679(2), b=8.073(2), c=19.292(4) Å, β=97.69(1)°, V=1948.2(7) Å^3, Z=4 for (BEDT-TTF)ReO_4(THF)$_{0.5}$, $(C_{10}H_8S_8)ReO_4(C_4H_8O)_{0.5}$.

Intensities were measured on a Rigaku automated diffractometer with Mo Kα radiation. The number of the independent reflections ($2\theta \le 60°$, $|F_o| > 3\sigma(|F_o|)$) of the ReO_4 salt is 2797 and that of the IO_4 salt is 1798. The small number of the observed reflections for the IO_4 salt is due to the poor quality of the crystal.

The structures were solved by the direct method and refined to conventional R values of 0.108 ((BEDT-TTF)ReO_4(THF)$_{0.5}$) and 0.122((BEDT-TTF)IO_4(THF)$_{0.5}$). Both the crystals are isomorphic. As shown in Fig. 1, there are four BEDT-TTF cations, four anions and two THF molecules in the unit cell. BEDT-TTF cations and anions are on the general positions and THF molecules are on the two-fold axis. Thermal parameters of the atoms in THF, the anions and the two ethylene groups suggest their large thermal motions (or positional disorders), which may be responsible for the relatively large R values. Except for the ethylene groups, BEDT-TTF cations are nearly planar. They take dimer structures. The dimeric arrangement has been also found in the neutral BEDT-TTF crystal. In the crystals of (BEDT-TTF)X(THF)$_{0.5}$, the dimers are arranged to form infinite chains along the b axis (Fig. 2). The mode of intradimer overlapping is similar to that observed in the neutral BEDT-TTF crystal (face-to-face overlapping) but there is no overlap between the dimers. The adjacent dimers are shifted along the direction perpendicular to the long axis of the molecule, which is suitable for reducing the steric repulsion of the ethylene groups. There are many short intermolecular S···S contacts in the dimeric chain (Fig. 2). However, there is almost no short contact between the adjacent chains, because the anions and THF molecules are located between them: only one S···S contact (3.63 Å) is slightly shorter than the corresponding van der Waals distance (3.70 Å). Thus the BEDT-TTF cations are considered to form quasi-1-D system along the b axis. Since the chain is composed of the dimers of mono-cations (BEDT-TTF$^+$), the 1-D band formed from the highest occupied molecular orbital (HOMO) of BEDT-TTF is completely filled and the system must be a semiconductor. This conclusion is consistent with the results of the resistivity measurements.[9)]

The bond lengths of the BEDT-TTF mono-cations averaged assuming D_{2h} symmetry are



(a)

(b)

Fig. 1. Crystal structure of (BEDT-TTF)$IO_4(THF)_{0.5}$.
(a) The a^* axis projection.
(b) The b^* axis projection.
Crystal structure of (BEDT-TTF)$ReO_4(THF)_{0.5}$ is almost the same except for the thermal ellipsoids of the atoms.

compared with those of the molecules with different formal charges (BEDT-TTF$^{+\rho}$: ρ=0, 1/2, 2/3)$^{3,5-8)}$ (Table 1). The bonds *a* and *d* are shortest when ρ=0 and *b* and *c* are shortest when ρ=1. The bond lengths of BEDT-TTF$^{+1/2}$ and BEDT-TTF$^{+2/3}$ take intermediate values. Since extended Huckel molecular orbital calculation shows that the highest occupied molecular orbital of BEDT-TTF has b_{1u} symmetry with nodal planes on all the C-S bonds.$^{12)}$ Therefore, the lengths of the bonds, *b* and *c* are considered to increase and those of *a* and *d* decrease with increasing ρ. Consequently, despite of the less accuracy of the bond lengths of BEDT-TTF mono-cation, the relation between bond lengths and

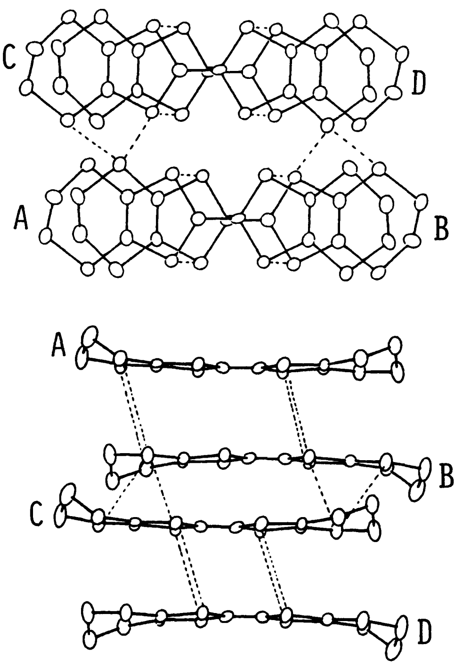
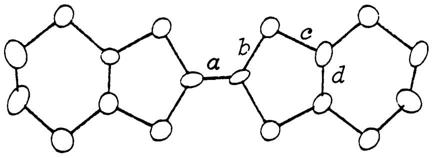


Fig. 2. Interdimer and intradimer arrangement of the molecules in (BEDT-TTF)X$(THF)_{0.5}$(X=ReO_4, IO_4). The dotted lines indicates the short S···S contacts (<3.6 Å).

ρ is consistent with the result of the molecular orbital calculation.

Table 1. Comparison of mean bond lengths of BEDT-TTF$^{+\rho}$.
The bond lengths are averaged by assuming D_{2h} symmetry.
The standard deviations are in the parentheses.

Formal charge (ρ) of BEDT-TTF(BEDT-TTF$^{+\rho}$)		Bond length (l/Å)10)				
ρ	(compound)	*a*	*b*	*c*	*d*	Ref.
0	neutral BEDT-TTF	1.312(12)	1.757(7)	1.754(8)	1.332(7)	5
1/2	α-$(BEDT\text{-}TTF)_2PF_6$	1.365(4)	1.740(2)	1.750(2)	1.345(3)	5,7
2/3	$(BEDT\text{-}TTF)_3(ClO_4)_2$	1.366(7)	1.731(7)	1.743(5)	1.345(9)	8
1	$(BEDT\text{-}TTF)ReO_4(THF)_{0.5}$	1.375(28)	1.719(10)	1.729(10)	1.365(18)	this work11)



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10) The bond lengths in the six-membered rings are less accurate because of the large thermal motion of the ethylene groups. They are not included in this Table.
11) The relatively accurate bond lengths of $(BEDT\text{-}TTF)ReO_4(THF)_{0.5}$ are adopted.
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