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CRYSTAL STRUCRTURE OF α-(BEDT-TTF)$_3$(ReO$_4$)$_2$

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The two-dimensional strucrture of α-(BEDT-TTF)$_3$(ReO$_4$)$_2$ on the (010) plane is very similar to that of (BEDT-TTF)$_3$(ClO$_4$)$_2$, although the three dimensional structure is quite different from each other. The slight geometrical difference between the crystallographically independent molecules suggests the different formal charge of these molecules.

We have studied the electronic specrtra of a series of the single crystals of bis(ethylenedithiolo)tetrathiafulvalenium(BEDT-TTF) salts to elucidate the band structure of these materials.1-4) In the process of our study, we found that the reflectance spectrum of α-(BEDT-TTF)$_3$(ReO$_4$)$_2$ is similar to that of (BEDT-TTF)$_3$(ClO$_4$)$_2$, although they are not isomorphous to each other. This material exhibits a metal-insulator transition at 88 K5) like (BEDT-TTF)$_3$(ClO$_4$)$_2$ which does at 170 K.6) This similarity of the two salts probably comes from the resemblance of their band structures. This is the motivation of the present structural study. Parkin et al. analyzed the crystal structures of a number of modifications of the ReO$_4$ salts of BEDT-TTF.5) However, they published only the lattice parameters and the figures projected on the (010) plane of α-(BEDT-TTF)$_3$(ReO$_4$)$_2$. In this letter, we present the details of the structural data of α-(BEDT-TTF)$_3$(ReO$_4$)$_2$.

The single crystals of α-(BEDT-TTF)$_3$(ReO$_4$)$_2$ were prepared in a tetrahydrofuran solution by using an electrochemical technique. The crystals were black and thin platelets developping the (010) crystal face. The intensities of X-ray diffraction were collected with a Rigaku automated diffractometer using a CuKα radiation monochromatized with a graphite plate. We obtained 3837 independent diffractions which have intensities larger than the statistical counting error, and used all of them for the analysis. The dimension of the crystal used in this measurement was 0.8 × 0.25 × 0.03 mm^3. The crystal belongs to the monoclinic system with the space group, $P2_1/n$, the lattice parameters being a =9.430(2), b =30.637(2), c =8.502(1) Å, β =98.73(1) , Z=2, V=2427.7 Å^3. The structure was solved by the direct method combined with the Monte-Carlo method[7)] for the selection of the initial set of phases. It was refined by the full-matrix least-squares method after applying the absorption corrections. The final R and R_w values were 0.073 and 0.081, respectively. The final atomic parameters were given in Table 1.

Table 1. Fractional atomic coordinates and equivalent temperature factors (Å^2)

	$x(\times10^4)$	$y(\times10^4)$	$z(\times10^4)$	B_{eq} a)		$x(\times10^4)$	$y(\times10^4)$	$z(\times10^4)$	B_{eq} a)
S1	5059(2)	-780(1)	-4113(3)	3.8	C5	3874(10)	570(3)	-1617(10)	3.4
S2	2110(2)	-682(1)	-5661(3)	3.8	C6	2484(10)	610(3)	-2298(10)	3.4
S3	4807(2)	122(1)	-2196(3)	3.8	C7	4357(14)	-2037(3)	-6505(15)	5.2
S4	1833(2)	214(1)	-3693(3)	3.9	C8	3322(12)	-1877(4)	-7939(14)	4.7
S5	5565(3)	-1626(1)	-5577(3)	4.1	C9	3544(12)	1275(3)	343(13)	4.5
S6	1986(3)	-1505(1)	-7434(3)	4.4	C10	2463(13)	1437(3)	-1079(13)	4.6
S7	4875(3)	908(1)	-230(3)	4.4	C11	55(9)	-184(3)	-441(11)	3.2
S8	1260(3)	1007(1)	-1932(3)	4.8	C12	917(10)	-899(3)	-1614(11)	3.5
S9	1576(2)	-512(1)	-153(3)	3.9	C13	-419(10)	-829(3)	-2381(11)	3.4
S10	-1339(2)	-365(1)	-1863(3)	3.7	C14	895(14)	-1738(4)	-2761(26)	8.2
S11	2066(3)	-1322(1)	-1876(3)	4.0	C15	-654(16)	-1683(4)	-2993(21)	6.9
S12	-1362(3)	-1170(1)	-3794(3)	4.6	Re	4554(1)	-2482(0)	-2002(1)	4.7
C1	3505(9)	-475(3)	-4318(10)	3.2	O1	4051(11)	-1964(3)	-2502(12)	6.5
C2	3398(9)	-90(3)	-3492(10)	3.2	O2	4962(10)	-2755(3)	-3654(11)	5.7
C3	4395(9)	-1199(3)	-5390(10)	3.3	O3	3149(17)	-2736(4)	-1321(14)	9.1
C4	2993(11)	-1153(3)	-6139(11)	3.6	O4	5996(19)	-2464(4)	-581(18)	9.8

a) $B_{eq} = (4/3)\Sigma_{ij}\beta_{ij}(a_i \cdot a_j)$.

Figure 1 shows the arrangement of the molecules viewed along the short molecular axis. The molecules were stacked along the [$\bar{1}$01] axis with the overlapping mode shown in Fig.2. The periodic unit is the BEDT-TTF triad which is composed of the molecules I, II, and I'. The molecule I is related to the molecule I' by a center of symmetry and the molecule II is on the center of symmetry. The intrastack contacts are longer than the sum (3.70 Å) of the Pauling's van der Waals radius of a sulfur atom. Figure 3 illustrates the arrangement on the (010) plane viewed nearly along the long molecular axis. Several S-S contacts shorter than 3.70 Å were observed along the [201] and [102] directions. This arrangement of BEDT-TTF on the (010) plane is similar to that on the (100) plane of the (BEDT-TTF)$_3$(ClO$_4$)$_2$ crystal. The characteristics of the structure on the (010) plane can be described by the angles between the stacking direction, [$\bar{1}$01], and the S-S directions, [201] and [102]. The angle is 76° between [$\bar{1}$01] and [102], and that is 115° between [$\bar{1}$01] and [201]. The corresponding angles on the (100) plane of the (BEDT-TTF)$_3$(ClO$_4$)$_2$ crystal are 81° between [0$\bar{1}$1] and [012], and 121° between [0$\bar{1}$1] and [021]. These molecular sheets on the (010) plane are separated from each other by the ReO$_4$ anions as illustrated in Fig.1. The stacking mode of the sheets along the *b*-axis is quite different from that of (BEDT-TTF)$_3$(ClO$_4$)$_2$, where the direction of the long axis of BEDT-TTF is parallel to each other. Although the three dimensional structure of α-(BEDT-TTF)$_3$(ReO$_4$)$_2$ is quite different from that of (BEDT-TTF)$_3$(ClO$_4$)$_2$, the electric and optical propereties are similar to each other. Since these properties are sensitive to the arrangement of molecules, this structure indicates the two-dimensionality of the electronic structures of these materials.

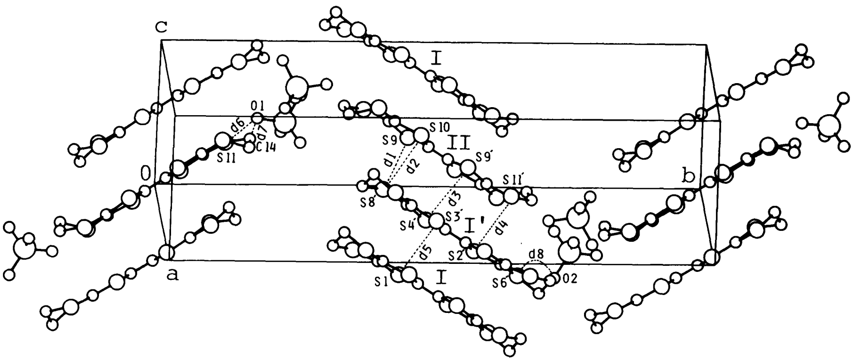


Fig. 1. Side view of the stack. The molecules I and I' are interrelated by the center of symmetry, and the molecule II is on the center of symmetry. The S-S distances shorter than 4.0 Å are d1=3.75, d2=3.77, d3=3.78, d4=3.77, and d5=3.75 Å. The interatomic distances shorter than the van der Waals contacts between BEDT-TTF and ReO_4 are d6=2.82, d7=3.03, and d8=3.04 Å.

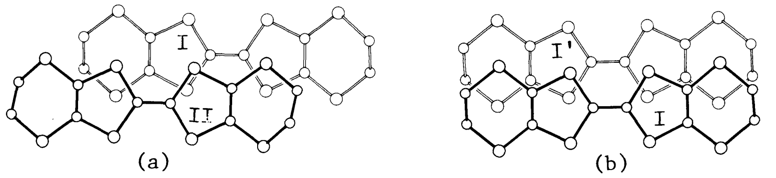


Fig. 2. Mode of the molecular overlap.

(a) molecules I and II
(b) molecules I and I'

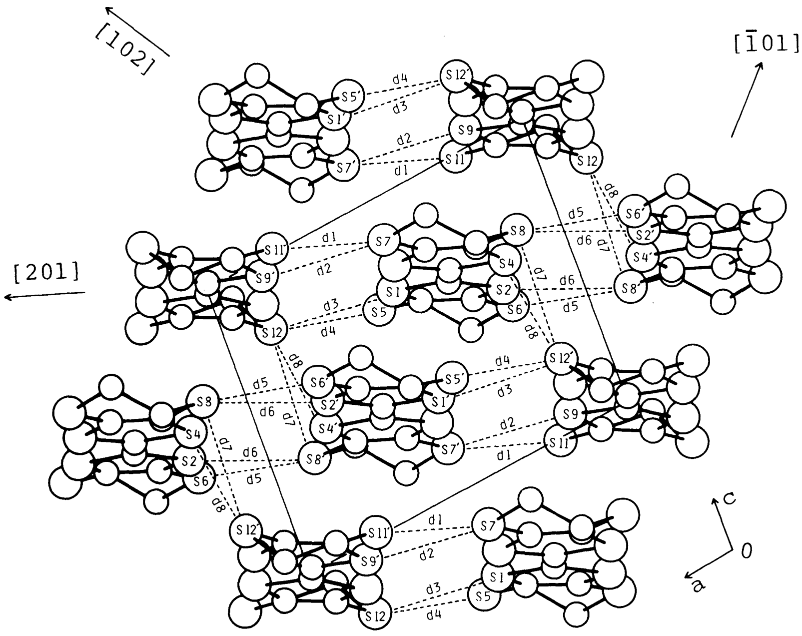
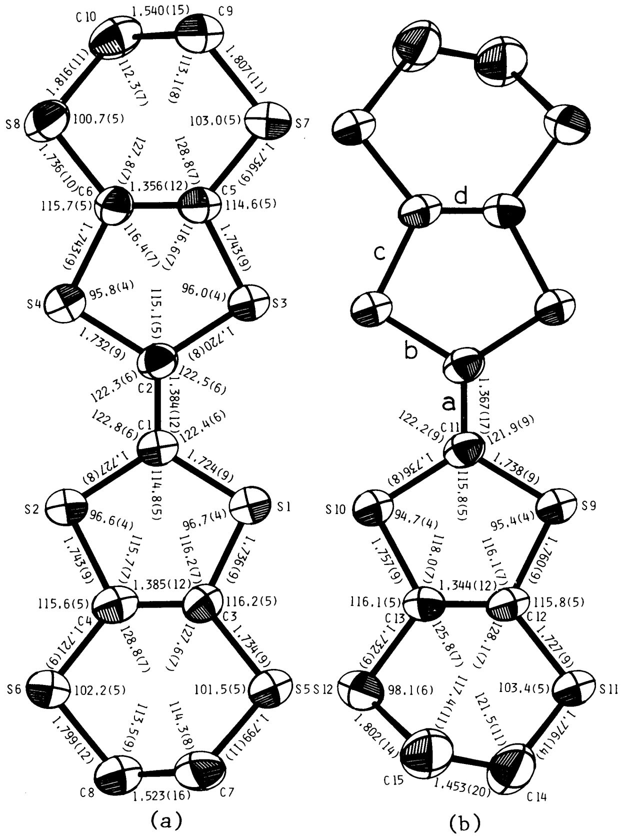


Fig. 3. Arrangement of the BEDT-TTF molecules in the (010) plane. The angle between [$\bar{1}$01] and [102] is 76° and that between [102] and [201] is 39°. The S-S distances shorter than the Pauling's van der Waals contacts are d1=3.40, d2=3.53, d3=3.55, d4=3.36, d5=3.39, d6=3.65, d7=3.68, and d8=3.61 Å.

The ReO_4 anion is nearly a tetrahedron, which has an average Re-O distance of 1.70 Å (1.68-1.73 Å) and an average O-Re-O angle of 109° (108-111°). We found short contacts between BEDT-TTF and ReO_4. The interatomic distances shorter than the van der Waals contacts are 3.04(1)Å for S6-O2, 2.82(1)Å for S11-O1, and 3.03(1)Å for C14-O1, which are illustrated in Fig.1. The geometries of the molecules are shown in Fig.4. The ethylene groups are out of the molecular plane in the molecule II, so that the molecule II has a chair-like conformation, while the carbon atoms in each ethylene group of the molecule I are located at the opposite side of the molecular plane, so that each C-C bond obliquely crosses the molecular plane. The average bond lengths of the TTF moiety are listed in Table 2. No significant difference could be found between the molecules I and II,



(a) (b)

Fig.4. Bond lengths and bond angles of BEDT-TTF. (a) molecule I, (b) molecule II

Table 2. Average bond lengths (Å) of BEDT-TTF

	$\rho^{a)}$	a	b	c	$d^{b)}$
(1)	0	1.312(12)	1.757(7)	1.754(8)	1.332(7)
(2)	1/2	1.365(4)	1.740(2)	1.750(2)	1.345(3)
(3)	2/3	1.365(8) 1.368(11)	1.733(18) 1.728(18)	1.744(13) 1.740(12)	1.345(13) 1.357(12)
(4)	1	1.38(3)	1.72(1)	1.73(1)	1.37(2)
(5)	I II	1.384(12) 1.367(17)	1.726(9) 1.737(9)	1.741(9) 1.759(9)	1.371(12) 1.344(12)

(1)BEDT-TTF, Ref.8, (2)α-(BEDT-TTF)$_2$PF$_6$, Ref.8
(3)(BEDT-TTF)$_3$(ClO$_4$)$_2$, Ref.9
(4)(BEDT-TTF)ReO$_4$(THF)$_{0.5}$, Ref.8
(5)α-(BEDT-TTF)$_3$(ReO$_4$)$_2$, this work
a)ρ is the formal charge of BEDT-TTF.
b)a-d indicate the average bond lengths defined in Fig.4.

since the standard deviation is fairly large. However, the systematic difference between the molecules I and II is more conspicuous than the corresponding difference in (BEDT-TTF)$_3$(ClO$_4$)$_2$. This suggests that the charge on the molecule I is more positive than that on the molecule II.

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