The Crystal Structure of $(TMTTF)_2ReO_4$

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Synopsis. The crystal of $(TMTTF)_2ReO_4$ is isomorphous with the other $(TMTTF)_2X$ compounds($X=ClO_4$, PF_6, Br,···). TMTTF molecules are stacked face-to face to form a zig-zag column. Although the structure of $(TMTTF)_2ReO_4$ closely resembles that of the analogous compound, $(TMTSF)_2ReO_4$, the loose intermolecular contacts in $(TMTTF)_2ReO_4$ suggest that the intermolecular interaction appears to be much weaker than that in $(TMTSF)_2ReO_4$.

It is well-known that tetramethyltetraselenafulvalene(TMTSF) forms a number of 2:1 salts with a variety of monovalent inorganic anions (Bechgaard salt). They exhibit a superconducting-phase transition and the charge (or spin)-density wave instability characteristic of one-dimensional metal systems.[1] Although the Bechgaard salts are isomorphic with each other, their physical properties are different from salt to salt and are sensitive to the small structural change induced by the variation in the anions. The sulfur analog, tetramethyltetrathiafulvalene (TMTTF), also form the isostructural series of $(TMTTF)_2X$ salts ($X=ClO_4$, PF_6, Br,···).[2] The band-structure calculation[3] shows that the Fermi surface of $(TMTTF)_2X$ is composed of distorted planes, quite similar to that of $(TMTSF)_2X$.[4] However, unlike $(TMTSF)_2X$, $(TMTTF)_2X$ undegoes a metal-insulator transition at a comparatively high temperature.[5] Recent studies have shown that $(TMTTF)_2Br$ and $(TMTTF)_2SCN$ take the antiferromagnetic ground states.[6,7]

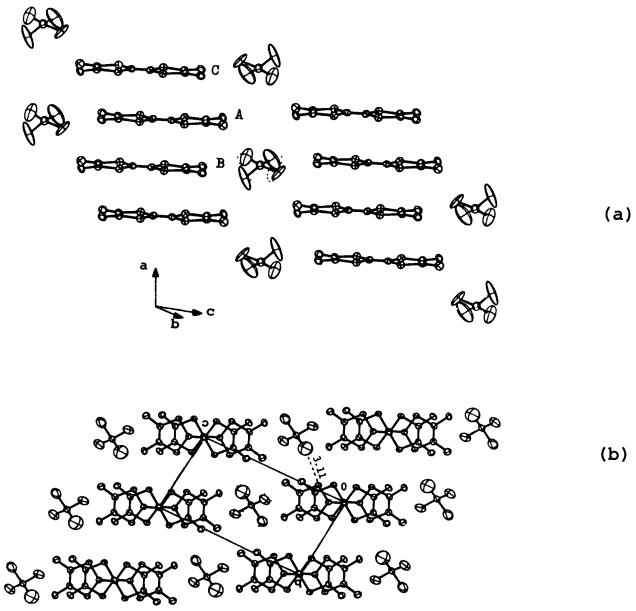

Fig. 1. (a) Side view of stack (tilted 10 °). The ReO_4 anions show disorder, taking one of the two possible positions randomly.
(b) View along *a*.

TABLE 1. FRACTIONAL COORDINATES AND ISOTROPIC TEMPERATURE FACTORS FOR $(TMTTF)_2ReO_4$

Atom	*x*	*y*	*z*	B_{eq}/Å^2
Re	0.0	0.5	0.5	4.8
S (1)	0.3539(5)	0.3122(4)	0.1073(2)	3.7
S (2)	0.2410(5)	−0.0639(4)	0.2105(2)	3.5
S (3)	0.2827(5)	0.1451(4)	−0.1111(2)	3.7
S (4)	0.1766(5)	−0.2306(4)	−0.0084(2)	3.7
C (1)	0.2756(17)	0.0750(15)	0.0957(9)	3.2
C (2)	0.2517(17)	0.0073(15)	0.0022(9)	3.1
C (3)	0.3621(19)	0.2915(16)	0.2393(10)	4.2
C (4)	0.3079(18)	0.1148(17)	0.2895(10)	3.9
C (5)	0.2232(17)	−0.0331(16)	−0.1914(9)	3.7
C (6)	0.1729(18)	−0.2093(16)	−0.1399(10)	3.8
C (7)	0.4297(20)	0.4665(18)	0.2920(10)	4.6
C (8)	0.3083(23)	0.0703(21)	0.4019(11)	5.1
C (9)	0.2317(20)	0.0206(19)	−0.3018(10)	4.3
C (10)	0.1157(19)	−0.3865(17)	−0.1913(11)	4.5
O (1)	0.0517(51)	0.3185(34)	0.4540(24)	16.1
O (2)	0.1463(82)	0.6313(42)	0.5670(28)	19.6
O (3)	0.0310(88)	0.4271(74)	0.5775(42)	16.7
O (4)	−0.0679(68)	0.3748(46)	0.6242(28)	16.2

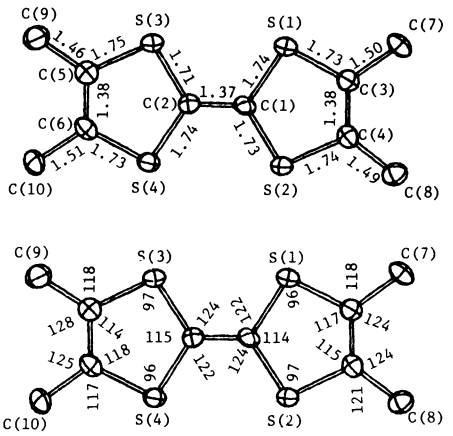

Fig. 2. The bond lengths (Å) and angles (°) of TMTTF. The averaged standard deviations of the bond lengths and angles are 0.02 Å and 1.3 °, respectively.

We also made structure analyses of $(TMTTF)_2X$ ($X=ClO_4$, ReO_4) and $(TMTSF)_2X$ ($X=BF_4$, ReO_4), $(TMTSF)_2BF_4$ structure of which has been previously reported.[8] However, we found that the structural description has been made on $(TMTSF)_2ReO_4$ and $(TMTTF)_2ClO_4$.[2,9] In this paper, we wish to report on the crystal structure of $(TMTTF)_2ReO_4$.

The black needle crystals were prepared electrochemically. The crystal data are: $(TMTTF)_2ReO_4$, $(C_{10}H_{12}S_4)_2ReO_4$, F.W.=771.1, triclinic, $P\bar{1}$, a=7.166(2), b=7.621(2), c=13.230(3) Å, α=86.62(2), β=95.56(2), γ=108.20(2)°, U=679.5(3) Å^3, Z=1, d_c=1.88 gcm^{-3}. The intensities were measured on a Rigaku automated diffractometer with Mo $K\alpha$ radiation up to 2θ=60°. The structure refinement gave a conventional R value of 0.066. The structure is shown in Fig. 1. The bond lengths and angles are given in Fig. 2. The atomic coordinates are given in Table 1. The table of the anisotropic temperature factors and F_o-F_c table are kept at the Chemical Society of Japan (Document No. 8421).

As has been mentioned before, $(TMTTF)_2ReO_4$ is isostructural with the other compounds of the $(TMTTF)_2X$ and $(TMTSF)_2X$ series. The planar TMTTF molecules are stacked face-to-face to from a zig-zag column along the a axis. Two independent interplanar distances are 3.57 (A···B) and 3.59 Å (A···C) (see Fig. 1). These values are somewhat larger than those of the other $(TMTTF)_2X$ salts:[2] 3.50, 3.53 Å (x=Br); 3.50, 3.57 (NO_3); 3.50, 3.54 (I); 3.54, 3.56 (BF_4); 3.49, 3.56 (SCN); 3.52, 3.59 (ClO_4); 3.53, 3.62 (PF_6). There appears to be a good correlation between the size of the anions and the interplanar distances. Although the $(TMTTF)_2X$ compound is considred to be a one-dimensional metal around room temperature, there is no short intermolecular contact along the columns. The shortest S···S distance in $(TMTTF)_2ReO_4$ (3.74 Å) is longer than the van der Waals distance of S···S (3.70 Å). Similarly, in the perchrolate salt, the shortest S···S distance is 3.73 Å.[10]

The short contact between Se stoms and the atoms of the anions is a common structural feature in $(TMTSF)_2X$ systems.[11] The shortest Se···O distance in $(TMTSF)_2ReO_4$ is 3.10 Å,[10] indicating a strong coupling between the TMTSF columns and the ReO_4 anions. This is consistent with the occurence of a sharp metal-insulator transition in $(TMTSF)_2ReO_4$, where the distortion of TMTSF columns and the displacement of ReO_4 anions take place cooperatively.[12] However, the shortest S···O contact in $(TMTTF)_2ReO_4$ is 3.12 Å, which is only slightly shorter than the corresponding van der Waals distance. The generous metal-insulator transition in $(TMTTF)_2X$[5] ($X=BF_4$, ClO_4, SCN,···) may be attributable to the loose contact between TMTTF columns and the anions. The preliminary resistivity measurement of $(TMTTF)_2ReO_4$ suggests the existence of a metal-insulator transition around 230 K, with the room-temperature resistivity of 0.03 Ω cm.

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