A new crystal structure for (BEDT–TTF)₂SbF₆ and some of its physical properties

G K R SENADEERA* and T MORI†

Institute of Fundamental Studies, Hantane Road, Kandy, Sri Lanka

†Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Tokyo 152-8552, Japan

MS received 26 October 2004; revised 14 December 2004

Abstract. A new crystal structure for *bis*(ethylenedithio)tetrathiafulvalene [(BEDT–TTF)₂SbF₆] was determined by single crystal X-ray diffraction. The crystal structure was refined in the $P\bar{1}$ space group at room temperature. Crystal data for new structure are as follows: triclinic, $a = 8.670$ (2) Å, $b = 8.664$ (2) Å, $c = 16.842$ (5) Å, $\alpha = 89^\circ.29$ (2), $\beta = 90^\circ.71$ (3), $\gamma = 92^\circ.67$ (1), $V = 1263.64$ Å³, $Z = 2$, $D_x = 2.136$ g cm⁻³, (Mo–K α), $I = 0.7107$ Å, $R = 0.057$ for a total of 5517 independent reflections. The donors form a trimerized column, and the band structure calculated by the tight-binding approximation shows band insulator properties. The temperature dependent of the d.c. resistivity shows a semiconducting behaviour with room temperature resistivity along the c -axis; $r_{290\text{ K}} = 5.6$ ohm cm.

Keywords. Organic conductors; b -(ET)₂PF₆; (ET)₂SbF₆; electrocrystallization.

1. Introduction

The *bis*(ethylenedithio)tetrathiafulvalene [BEDT–TTF (or ET)]; salts are one of the recent additions to the organic superconductors family. One of the characteristic features of these materials is the ability to exhibit large number of crystal types and polymorphism. Moreover, different kinds of crystal structures can be found from the same anion and solvent with the same composition and also with vastly different physical property (Williams 1991). Among these ET salts, a and b -(ET)₂PF₆ complexes are the earliest reported ET based materials. This b -(ET)₂PF₆ undergoes a metal insulator transition at 297 K (Kobayashi *et al* 1983a). It has been reported that b -(ET)₂PF₆ and (ET)₂X ($X^- = \text{AsF}_6^-, \text{SbF}_6^-$) complexes have very similar donor molecule packing motif (Williams 1991). Furthermore, these two AsF₆⁻ and SbF₆⁻ complexes undergo similar transition at 273 and 264 K, respectively (Sekretarczyk *et al* 1986). The room temperature crystal structure reported for (ET)₂SbF₆ is monoclinic, $I2/c$ space group with following lattice parameters; $a = 33.56$ Å, $b = 6.70$ Å, $c = 14.4$ Å, $\beta = 90^\circ.71$ (Larversenne *et al* 1984). However, in the process of studying the metal–insulator transition of this family of complexes, we found for the first time another possible new crystal structural data for (ET)₂SbF₆ complex which is reported here with some of its electrical properties.

2. Experimental

2.1 Synthesis and crystal growth

Crystals of (BEDT–TTF)₂SbF₆ were obtained by means of electrocrystallization. Commercial grade 1,1–2-trichloroethane was purified by chemical treatment and distilled prior to use as solvent. Recrystallized BEDT–TTF from 1,1–2-trichloroethane was used as the donor and (nBu₄N)SbF₆ was used as the counter anion. The solution concentrations used for crystal growth were as follows. 14 mg of donor molecule was added to the anode compartment of the standard cell used in the electrocrystallizations. Then 80 mg of (nBu₄N)SbF₆ was weighed and separated into two portions (3 : 1). The big portion was put into the anode compartment of the cell and the rest to cathode compartment. 35 ml of solvent was measured and added to both compartments of the cell until getting equal levels. Pt electrodes were inserted into the cell and then purged with Ar. Then the mixtures were stirred by sonicating for some time until the salts got completely dissolved. Finally the cell was connected to an external power supply. Constant current of 1 μ A was used throughout the crystallization and crystals were grown at controlled temperature (299 K). Black, thin plate-like crystals were obtained. The period of the crystal growth was about 2 weeks.

2.2 Crystal structure determination

X-ray unit cell determination and data collection were performed with a Rigaku Raxis II single crystal diffracto-

*Author for correspondence (rsena@ifs.ac.lk)

Table 1. Crystal data collection and refinement parameters of (BEDT-TTF)₂SbF₆.

Chemical formula	C ₁₅ H ₁₂ S ₁₂ SbF ₆
<i>F</i> (Weight)	812.72
System	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> (Å)	8.670 (29)
<i>b</i> (Å)	8.664 (2)
<i>c</i> (Å)	16.842 (5)
<i>a</i>	89.29 (2)
<i>b</i>	90.71 (3)
<i>g</i>	92.67 (1)
<i>V</i> (Å ³)	1263.64 (10)
<i>Z</i>	2
<i>R</i>	0.06
<i>D_c</i> (g cm ⁻³)	2.26
<i>T</i>	288
<i>2q_{max}</i>	60
MoKα, 1/Å	0.7107
No. of measured refl.	5517
No. of observed refl.	4165
Parameters	307
Colour	Black

meter with Mo-Kα radiation. The structure was solved by use of direct methods (SHELX86), followed by least square refinements and differential Fourier maps. The final full matrix least squares structure refinement of 307 variable parameters were done using 5517 reflections [$2\theta < 60.1^\circ$ (Mo-Kα)] with full matrix least value of 0.057. Details of the structure analysis followed are given elsewhere (Mori *et al* 1985, 1986).

2.3 Electrical resistivity measurements

The temperature dependence of electrical resistivity was measured in the range 220–350 K, on single crystal by using standard four-probe technique. The electrical contacts on crystals were made by gold wires with diameter of 0.25 μm using gold paints (Mori *et al* 1986).

2.4 Band structure calculations

The overlap integrals of the highest occupied molecular orbital level (HOMO) and the band structure were calculated as described elsewhere (Mori *et al* 1986).

Table 2. Fractional atomic coordinates and equivalent isotropic thermal parameters of (BEDT-TTF)₂SbF₆.

Atom	<i>x</i> (Å)	<i>y</i> (Å)	<i>z</i> (Å)	<i>B_{eq}</i>
Sb()	0.85003(8)	0.35010(8)	0.49999(4)	4.72 (1)
S(1)	1.1005(3)	0.6916(3)	1.1802(1)	5.25(6)
S(2)	0.8087(3)	0.3994(3)	1.1802(1)	5.29(6)
S(3)	0.9559(2)	0.7890(2)	1.1803(1)	3.39(4)
S(4)	0.7111(2)	0.5443(2)	1.0301(1)	3.39(4)
S(5)	0.8446(2)	0.9008(2)	1.0301(1)	3.39(4)
S(6)	0.5991(2)	0.6556(2)	0.8554(1)	3.42(4)
S(7)	0.8008(3)	0.9893(3)	0.8555(1)	4.43(5)
S(8)	0.5106(3)	0.6995(3)	0.6865(1)	4.45(5)
S(9)	0.7940(3)	0.9984(4)	0.6865(1)	5.94(7)
S(10)	0.5016(4)	0.7057(3)	1.2474(2)	5.86(7)
S(11)	0.6742(3)	1.0684(3)	1.2474(2)	4.13(5)
S(12)	0.4315(3)	0.8261(3)	1.0879(1)	4.08(5)
F(1)	0.906(2)	0.251(2)	1.0880(1)	16.6(5)
F(2)	0.750(2)	0.408(2)	0.4110(5)	16.9(5)
F(3)	0.9643(10)	0.2217(10)	0.5637(5)	10.3(3)
F(4)	0.720(1)	0.4658(10)	0.4373(5)	10.4(3)
F(5)	0.692(1)	0.196(1)	0.5001(8)	15.4(4)
F(6)	1.026(4)	0.496(4)	0.452(2)	41(1)
C(1)	1.0572(2)	0.555(2)	1.2528(7)	10.0(4)
C(2)	0.946(2)	0.444(1)	1.2529(7)	9.1(4)
C(3)	0.9543(8)	0.6572(8)	1.1097(4)	3.0(1)
C(4)	0.8415(8)	0.5459(8)	1.1096(4)	2.9(1)
C(5)	0.8006(8)	0.7002(8)	0.9793(4)	2.6(1)
C(6)	0.7523(8)	0.7474(8)	0.9068(4)	2.6(1)
C(7)	0.7409(9)	0.8722(8)	0.7659(4)	2.8(1)
C(8)	0.6282(8)	0.7597(8)	0.7662(4)	2.8(1)
C(9)	0.731(2)	0.876(2)	0.6050(6)	9.0(4)
C(10)	0.624(2)	0.768(2)	0.6052(6)	9.0(4)
C(11)	0.720(2)	0.893(2)	1.3292(6)	8.6(4)
C(12)	0.606(2)	0.780(2)	1.3294(6)	8.4(4)
C(13)	0.6589(9)	0.9553(9)	1.1732(4)	3.4(2)
C(14)	0.5443(9)	0.8416(9)	1.1733(4)	3.5(2)
C(15)	0.5234(9)	0.9767(9)	1.0367(4)	3.3(2)

3. Results and discussion

The X-ray crystal data collection parameters are summarized in table 1. The atomic coordinates and the equivalent isotropic thermal parameters are listed in table 2. While figure 1(A) shows the atomic numbering schemes of the two crystallographically independent BEDT-TTF molecules of the unit cell, figure 1(B) illustrates the atomic numbering scheme of the (SbF₆)²⁻ counter ion. Two SbF₆⁻ units share two F atoms, thus the anion unit is Sb₂F₁₂²⁻ and a Sb atom is coordinated by seven F atoms. There is an inversion centre at the centre of the two Sb atoms. The mode of the donor molecular arrangement is shown in figure 2(A). The donor molecules display *ABA* type of molecular arrangement. There are one and half units of crystallographically independent BEDT-TTF molecules; the molecule *A* is located on a general position and another half is located on an inversion centre. An anion unit, SbF₆⁻, is located on a general position, thereby the composition is (BEDT-TTF)₃(SbF₆)₂. Figure 2(B) shows a schematic view of the mode of two different overlappings; (a) A-B molecules (p2), and (b) A-A molecules (p1). Figure 2(C) shows the crystal structure of new (BEDT-TTF)₂SbF₆. The triclinic donor cell contains three donor molecules. The BEDT-TTF cations are arranged in face-to-face stacks parallel to the *a*-*b* axis. The anions are coated in an "anion cavity" formed by the ethylene groups of the donor molecules and thus isolate the stacks in the *c*-

direction. Within the stacks, the donor molecules are nearly parallel to the *c* axis and normal to the *ab* plane as shown in the figure. Table 3 tabulates the intermolecular overlap integrals between donors (as shown in figure 2(D)), calculated based upon the extended Hückel method (Kobayashi *et al* 1983b). The interaction, p2, between B-A

Figure 1. (A) Atomic numbering schemes of the two crystallographically independent BEDT-TTF molecules ((a), (b)) and (B) atomic numbering scheme of the (SbF₆)²⁻ counterion.

Figure 2. (A) The mode of the donor molecular arrangement of (BEDT-TTF)₃(SbF₆)₂, (B) schematic view of the mode of two different overlappings: (a) A-B molecules (p2), and (b) A-A molecules (p1), (C) crystal structure of (BEDT-TTF)₃(SbF₆)₂ projected on the *bc* plane and (D) intermolecular overlaps in (BEDT-TTF)₃(SbF₆)₂.

Figure 3. (A) Tight-binding energy band structure of $(\text{BEDT-TTF})_3(\text{SbF}_6)_2$ and (B) temperature dependence of normalized resistivity for the new SbF_6 salt at ambient pressure: (a) linear plot and (b) Arrhenius plot.

molecules (independent donor molecules) are much larger than that between the equivalent molecules (A–A), p1. This is because the displacement for p1 (A–A) is large ($D = 4.0 \text{ \AA}$), whereas p2 (A–B) is made of a nearly eclipsed overlap ($D = 0.5 \text{ \AA}$) (see figure 2A). Therefore, ABA unit makes a trimer. Figure 3(A) depicts the energy band structure calculated by tight-binding approximation. The band is separated into three bands, due to the trimerization. According to this, the energy gap exists at the Fermi level, therefore, no Fermi surface appears. This indicates that this material is a band insulator. Figure 3(B) (a) illustrates the temperature dependence of the resistivity of $(\text{ET})_2\text{SbF}_6$ at ambient pressure. The room temperature value of the electrical resistivity, $r_{290\text{ K}}$, is about 5.6 ohm cm . The resistivity measurement shows that the material is also a semiconductor with the average activation energy, $E_a = 0.25 \text{ eV}$, calculated from the plot of $\ln(r_T)$ vs $1/T$ between 238 K and 315 K as shown in figure 3(B) (b).

Table 3. Inter molecular overlap integrals in $(\text{BEDT-TTF})_2\text{SbF}_6$, the parameter f ; the angle between the molecular plane and the interaction direction, and D ; the slip distance along the molecular long axis, describing the configuration of the neighbour molecules, as defined in figure 2.

	$S (10^{-3})$	f	$D (\text{\AA})$
p1	8.6	90°	4.0
p2	– 20.8	90°	0.6
q1	– 4.8	58°	3.1
q2	8.7	18°	2.0
q3	4.8	16°	1.5
q4	4.9	66°	7.2

4. Conclusions

A possible new crystal structure was observed for $(\text{BEDT-TTF})_2\text{SbF}_6$. The tight binding energy band calculations and molecular overlap integrals were determined. Tem-

perature dependence of the electrical resistivity showed a semiconducting behaviour. In contrast to the previously reported SbF₆ salt having 2 : 1 composition the present salt has 3 : 2 composition. The 3 : 2 composition is not unusual in BEDT-TTF salts. The well-known examples are (BEDT-TTF)₃(ClO₄)₂ and its analogs (Kobayashi *et al* 1984). These salts, however, have *b''* structure. *b*-like three-fold structure has been recently reported in (BEDT-TTF)₃Cl (pBIB), but with 3 : 1 salt (Yamamoto 1998). Furthermore, overlap mode of the trimer in the present salt is eclipsed configuration (*D* = 0.5 Å). Eclipsed overlap is quite rare in BEDT-TTF salts, and has been found only in *a*-(BEDT-TTF)₂PF₆ and (BEDT-TTF)₃Li_{0.5} Hg (SCN)₄(H₂O)₂ (Geiser *et al* 1990; Mori *et al* 1991). Therefore, the structure type is an entirely new one, which has no analog among the reported BEDT-TTF salts.

Acknowledgement

(GKRS) gratefully acknowledges financial support from UNESCO/MOMBUSHO programme to work at Tokyo Institute of Technology.

References

- Geiser U *et al* 1990 *Mol. Cryst. Liq. Cryst.* **181** 105
Kobayashi H, Mori T, Kato R, Kobayashi A, Sasaki Y, Saito G and Inoki H 1983a *Chem. Lett.* 581
Kobayashi H, Kobayashi A, Sasaki Y, Saito G and Inokuchi H 1983b *J. Am. Chem. Soc.* **105** 297
Kobayashi H, Kato R, Mori T, Kobayashi A, Sasaki Y, Saito G, Enoki T and Inokuchi H 1984 *Chem. Lett.* 179
Larversenne R, Amiell J, Delhaes P, Chasseau D and Hauw C 1984 *Solid State Commun.* **52** 177
Mori T, Kobayashi A, Sasaki Y, Kato R and Kobayashi H 1985 *Solid State Commun.* **53** 627
Mori T, Sakai F, Sato G and Inokuchi H 1986 *Chem. Lett.* 1589
Mori H, Tanaka S, Mori T, Maruyama Y, Inokuchi H and Saito G 1991 *Solid State Commun.* **78** 49
Sekretarczyk G, Krupiki M, Graja A, Delhaes P and Larversenne R 1986 *Physica* **B143** 547
Williams J L 1991 *Organic superconductors: synthesis, structure, properties and theory* (Englewood Cliffs, NJ: Prentice-Hall)
Yamamoto H M, Yamamura J and Kato R 1998 *J. Mater. Chem.* **1** 15