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Crystal Structures of Cation-Radical Salts of a Bis(1,3-dithiole) Donor Containing a 1,2,5-Thiadiazole Unit

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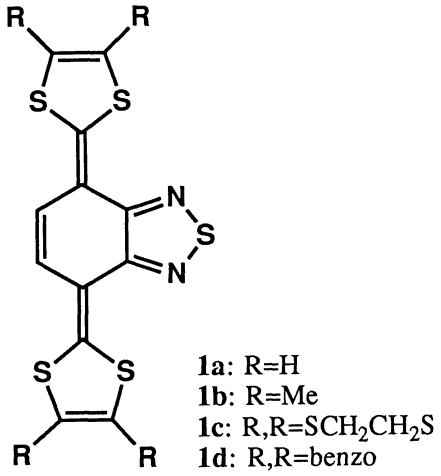
X-Ray analyses of PF_6 and BF_4 cation-radical salts of 4,7-bis(4,5-dimethyl-1,3-dithiol-2-ylidene)-4,7-dihydro-2,1,3-benzothiadiazole reveal that the PF_6 salt showing a metallic behavior has a uniform stacking of donor molecules, while the BF_4 salt showing a semiconducting behavior has a dimeric structure.

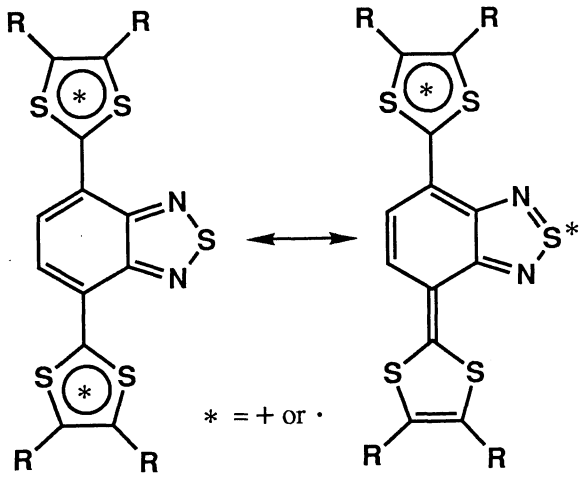
Tetrathiafulvalene (TTF) analogues with extended π-conjugation are promising electron donors for organic conductors.[1] Although a lot of bis(1,3-dithiole) donors have been synthesized, it is usually difficult to prepare the single crystals of highly conducting cation-radical salts and there are few reports on their crystal structures.[2] We report here the crystal structures of metallic and semiconductive cation-radical salts of a bis(1,3-dithiole) donor and discuss a relationship between the crystal structures and conducting properties.

We have recently prepared bis(1,3-dithiole) compounds **1a-d** containing a fused 1,2,5-thiadiazole ring as strong electron donors.[3] Among them only tetramethyl derivative **1b** gave highly conducting cation-radical salts as single crystals (σ/S cm^{-1} at room temperature ClO_4 salt; 16, BF_4 salt; 23, PF_6 salt; 110, AsF_6 salt; 68) whose molar ratios are all 2 : 1 (donor : anion). The PF_6 and AsF_6 salts showed metallic temperature dependence down to 100 K, while the ClO_4 and BF_4 salts showed semiconductive behaviors.[3] We have now carried out the X-ray analyses of the metallic PF_6 and semiconductive BF_4 salts to clarify the difference depending on counteranions.

The single crystals of the PF_6 and BF_4 salts were obtained as needles by an electrochemical oxidation of **1b** in dichloromethane containing Bu_4NPF_6 or Bu_4NBF_4 using platinum electrodes at 1 $\mu A/cm^2$. The crystals



1a: R=H
1b: R=Me
1c: R,R=SCH_2CH_2S
1d: R,R=benzo



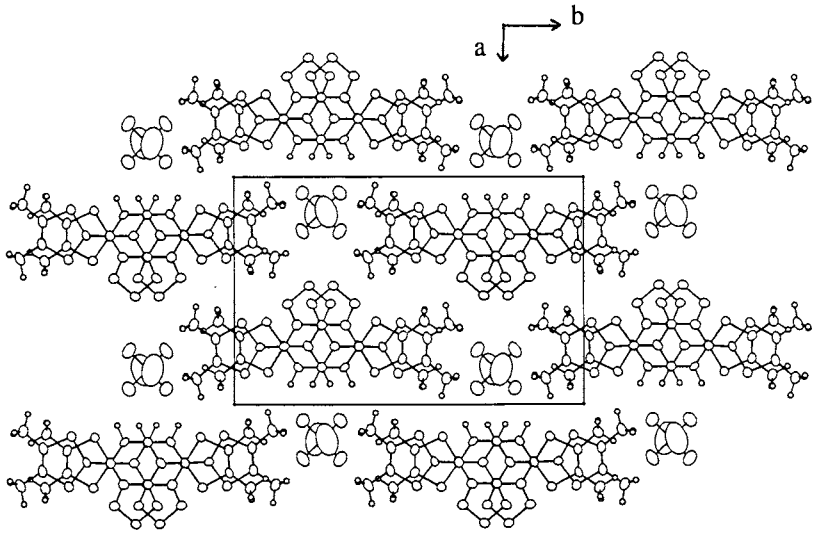


Fig. 1. Crystal structure of $(\mathbf{1b})_2PF_6$.

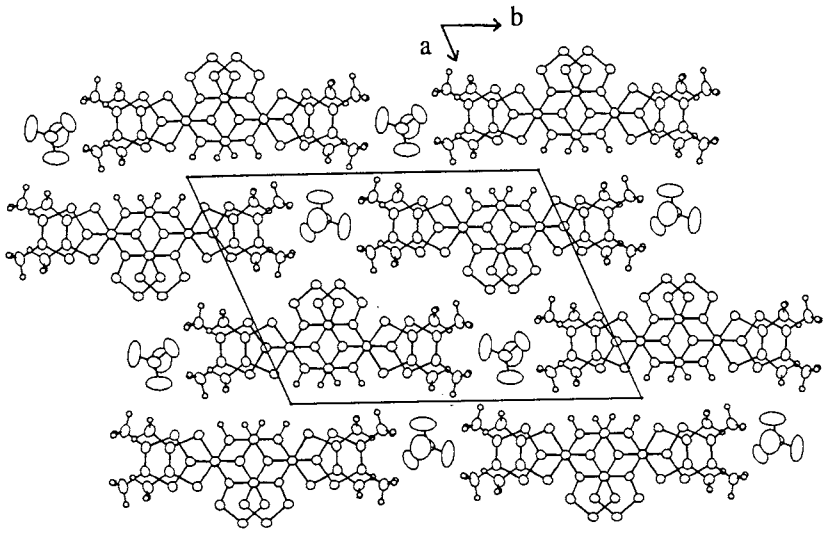


Fig. 2. Crystal structure of $(\mathbf{1b})_2BF_4$.

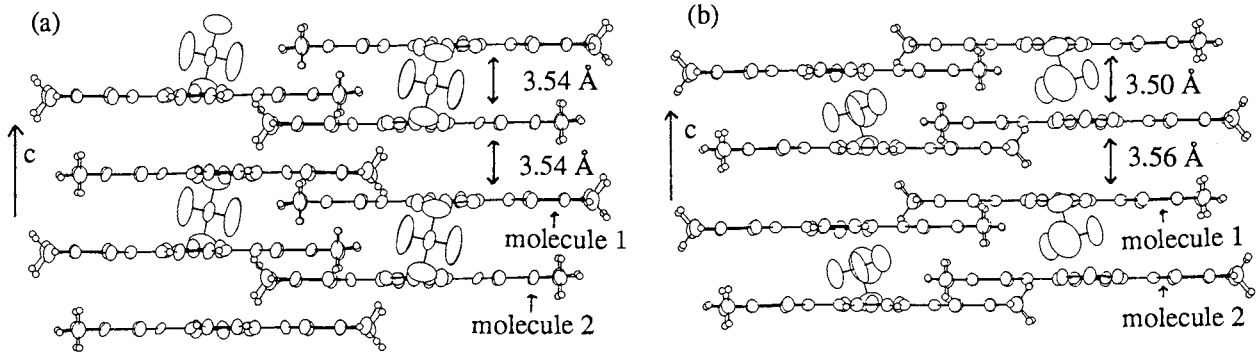
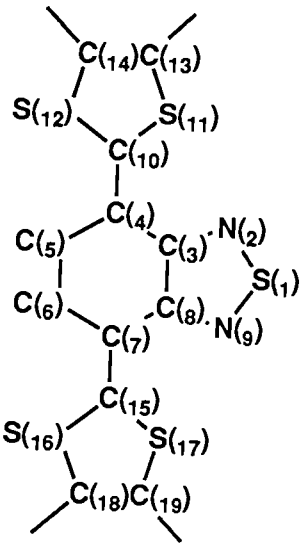


Fig. 3. Stacking modes along the c axis. (a); $(\mathbf{1b})_2PF_6$, (b); $(\mathbf{1b})_2BF_4$.

Table 1. Selected bond lengths (Å)

	(**1b**)$_2$PF$_6$		(**1b**)$_2$BF$_4$		**1d**
Bond	Molecule 1	Molecule 2	Molecule 1	Molecule 2	
S(1)-N(2)	1.627(8)	1.628(8)	1.630(5)	1.629(5)	1.641(4)
N(2)-C(3)	1.313(11)	1.336(11)	1.335(9)	1.341(8)	1.330(5)
C(3)-C(4)	1.438(12)	1.429(13)	1.434(8)	1.427(9)	1.451(6)
C(3)-C(8)	1.454(13)	1.430(13)	1.435(7)	1.430(7)	1.438(6)
C(4)-C(5)	1.423(12)	1.453(12)	1.449(9)	1.433(8)	1.454(6)
C(5)-C(6)	1.363(13)	1.362(12)	1.362(7)	1.371(7)	1.348(6)
C(6)-C(7)	1.452(12)	1.431(12)	1.428(8)	1.427(9)	1.454(6)
C(7)-C(8)	1.444(12)	1.428(12)	1.439(9)	1.427(8)	1.451(6)
C(8)-N(9)	1.309(12)	1.334(11)	1.330(8)	1.344(9)	1.333(5)
N(9)-S(1)	1.639(8)	1.633(8)	1.629(5)	1.632(5)	1.638(4)
C(4)-C(10)	1.398(13)	1.389(12)	1.390(7)	1.412(7)	1.361(6)
C(10)-S(11)	1.728(9)	1.726(9)	1.731(7)	1.715(6)	1.746(4)
S(11)-C(13)	1.733(9)	1.743(10)	1.754(6)	1.738(6)	1.761(4)
C(13)-C(14)	1.311(13)	1.320(14)	1.343(10)	1.357(10)	1.393(6)
C(14)-S(12)	1.752(9)	1.751(9)	1.749(6)	1.740(5)	1.746(4)
S(12)-C(10)	1.719(9)	1.731(9)	1.730(6)	1.428(7)	1.756(4)
C(7)-C(15)	1.397(12)	1.396(12)	1.386(7)	1.398(7)	1.365(6)
C(15)-S(16)	1.731(9)	1.731(9)	1.736(7)	1.719(6)	1.754(4)
S(16)-C(18)	1.741(9)	1.751(9)	1.747(5)	1.741(6)	1.745(4)
C(18)-C(19)	1.299(14)	1.321(13)	1.338(10)	1.339(10)	1.405(6)
C(19)-S(17)	1.752(9)	1.745(9)	1.748(6)	1.741(6)	1.754(4)
S(17)-C(15)	1.727(9)	1.720(9)	1.733(6)	1.722(7)	1.751(4)



have the same space group $P\bar{1}$ (triclinic).[4] The crystal structures are shown in Fig. 1 and Fig. 2. Because of Z=2 for the space group $P\bar{1}$, there exist two crystallographically independent donor molecules (molecule 1 and molecule 2) in their crystals. The molecules are planar and have short intramolecular contacts between the S of the dithiole and the N of the thiadiazole [(**1b**)$_2$PF$_6$: molecule 1; 2.816(8), 2.850(8) Å, molecule 2; 2.809(8), 2.856(8) Å, (**1b**)$_2$BF$_4$: molecule 1; 2.816(4), 2.823(5) Å, molecule 2; 2.801(5), 2.852(4) Å]. These values are almost the same with those of neutral **1d** [2.810(4) and 2.834(4) Å].[3] The selected bond lengths of the molecules are summarized in Table 1 along with those of neutral **1d**. The cation radical of **1b** is considered to be stabilized by resonance contributions **2'** and **2"**. The fact that the C(5)-C(6) bond lengths of the donor molecules in the salts are longer than that of neutral **1d** suggests the contribution of a resonance structure **2'** in the cation radical state of **1b**. On the other hand, the shorter S(1)-N(2) and C(3)-C(4) bond lengths in the salts compared with those of **1d** suggest the contribution of **2"**.

The crystal structures of the PF$_6$ and BF$_4$ salts are very similar to each other. There exist no short inter-heteroatom contacts such as S---N and S---S interactions. The counteranions are located in the cavities produced by donor molecules. Although there is a small difference in the structures as to the arrangement of donor molecules to form the cavities, the methyl substituents sandwich the anions in both crystals. The similar location of anions surrounded by methyl substituents is observed in the cation radical salts of tetrametylTTF (TMTTF)[5] and tetramethyltetraselenafulvalene (TMTSF).[6] This situation of counteranions may be favorable for formation of good single crystals since other derivatives **1a, c, d** have not afforded good crystals of the cation-radical salts.

The donor molecules in the crystals are stacked along the c-axis. The overlapping modes are the same in both crystals as shown in Fig. 1 and Fig. 2, where the 1,3-dithiole rings overlap in a similar manner as those in TMTTF and TMTSF salts.[5,6] However, a significant difference is seen in the stacking modes as shown in Fig. 3. The donor molecules in the PF_6 salt are stacked with an equal intermolecular distance of 3.54 Å although two kinds of molecules are stacked alternately (Fig. 3-(a)). In contrast the BF_4 salt has different interplanar distances of 3.50 and 3.56 Å, resulting in a dimeric structure (Fig. 3-(b)). The PF_6 salt taking a uniform stacking is metallic, while the BF_4 salt having a dimeric structure is semiconductive. This result confirms that a uniform stacking is essential for occurrence of a metallic property in one-dimensional conductors.[7] The difference depending on the counteranions seems to be ascribed to the shape of the anions since PF_6^- is an octahedral anion while BF_4^- is a tetrahedral anion. This is supported by the fact that (**1b**)$_2AsF_6$ having an octahedral anion shows a metallic behavior while (**1b**)$_2ClO_4$ having a tetrahedral anion is semiconductive. Symmetrical octahedral anions may be favorable for taking a uniform stacking due to the good packing.

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4) Crystal data for (**1b**)$_2PF_6$: triclinic, space group $P\bar{1}$, a=13.560(3), b=20.180(4), c=7.075(1) Å, α=96.84(1), β=105.14(1), γ=88.24(1)°, V=1855.5(6) Å^3, Z=2, D_{calcd}=1.67 g cm^{-3}. The final R value is 0.1017 for 4364 reflections with $|Fo| > 3\sigma|Fo|$. (**1b**)$_2BF_4$: triclinic, space group $P\bar{1}$, a=14.045(1), b=19.823(1), c=7.068(1) Å, α=84.01(1), β=91.87(1), γ=66.93(0)°, V=1794.7(3) Å^3, Z=2, D_{calcd}=1.62 g cm^{-3}. The final R value is 0.0652 for 4852 reflections with $|Fo| > 3\sigma|Fo|$.

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