

# Preparation and Structures of Dication Salts of Phenyl-Substituted TTF Vinylogues

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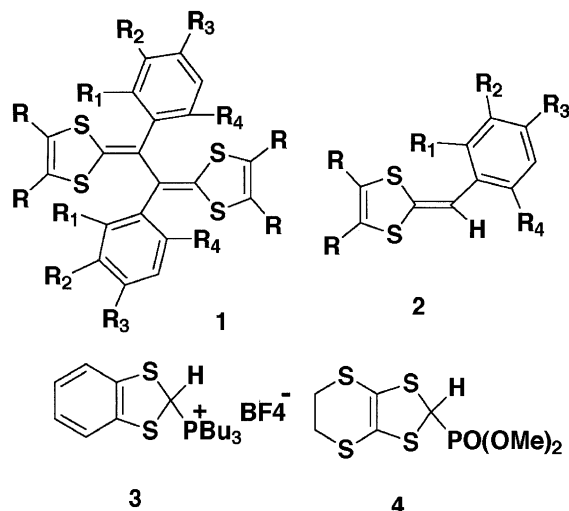
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Some TTF vinylogues **1** containing phenyl groups at the vinyl positions were synthesized. The redox properties were investigated by cyclic voltammograms, showing that they are strong electron donors and the Coulomb repulsion is decreased in the dication states. Some of the donors afforded their dication salts as single crystals by electrochemical oxidation or the reaction with  $\text{CuCl}_2$ . X-ray structure analysis has revealed that the dication molecules have structures with planar TTF vinylogue units and twisted phenyl groups. The crystal structures are unusual to avoid the steric interactions of the phenyl groups. © 2002 Elsevier Science (USA)

## INTRODUCTION

TTF vinylogues **1** are strong electron donors and exhibit small on-site Coulomb repulsion owing to the extended  $\pi$ -conjugation (1). The derivatives containing substituents at the vinyl positions have been synthesized by oxidative coupling reaction of 1,4-dithiafulvenes **2** (2). We have prepared TTF vinylogues **1** with various phenyl substituents by a chemical oxidation (3a). The redox behaviors are strongly affected by the substituents on the phenyl and the cation radical states of the derivatives bearing *ortho*-substituted phenyl groups are thermodynamically stable (3). Actually, some cation radical salts were obtained as single crystals, where the donor molecules have a planar TTF vinylogue skeleton and the phenyl groups are twisted and almost orthogonal to the TTF vinylogue plane (3–6). Owing to the steric interactions of the phenyl groups, the crystal structures are unusual. For example, the cation radical salt **1b**· $\text{PF}_6^-$  has a two-dimensional columnar structure, where one donor molecule bridges two others to avoid steric interactions (3a, 5). In the **1h**· $\text{Au}(\text{CN})_2^-$

crystal, the anions are sandwiched between the donor molecules (4). We have also reported that the derivatives of **1** containing hydroxyphenyl groups afford cation radical salts with unusual crystal structures involving hydrogen bonding between the OH group and the counteranions (6). These results show that the TTF vinylogues **1** with bulky groups at the vinyl positions are promising electron donors which afford conductors with unusual multi-dimensional structures. They are also expected to afford stable dication salts with unusual crystal structures because the Coulomb repulsion in the dication states are decreased due to the extended  $\pi$ -conjugation. Some dication salts have actually been isolated and X-ray analysis revealed that the molecular structures are similar to those of the cation radicals (7). In addition, it is possible to incorporate magnetic metal ions in the dication chathlates, which are interesting as organic–inorganic hybrids showing magnetic properties. We report here the synthesis and structures of the novel dication salts of **1**, some of which include Cu ions.



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## EXPERIMENTAL

*Preparation of Compounds*

TTF vinylogues **1a-c**, **g**, **h**, **l** were prepared by oxidative coupling reaction of the corresponding 1,4-dithiafulvalenes **2** (3a). According to this method, new compounds **1d-f**, **i-k** were synthesized in moderate yields. Thus, benzodithiafulvalenes **2d-f** were obtained by the Wittig reaction of a phosphonium salt **3** with the corresponding benzaldehydes. The ethylenedithio derivatives **2i-k** were prepared by the Wittig–Horner reaction of a phosphonium ester **4** with the corresponding benzaldehydes. Oxidative coupling reaction of **2** was achieved by using tris(4-bromophenyl)aminium hexachloroantimonate as an oxidation reagent followed by reduction of the resulting dications with zinc. The typical examples are as follows.

*Synthesis of 1e*

An excess amount of sodium hydride (60% in mineral oil, 60 mg, 1.5 mmol) was added to a solution of **3** (265 mg, 0.600 mmol) and 4-cyanobenzaldehyde (71 mg, 0.542 mmol) in dichloromethane (6 mL). The mixture was stirred for 30 min and after careful addition of H<sub>2</sub>O, the product was extracted with dichloromethane. Evaporation of the solvent followed by crystallization with ethanol gave a yellow solid of **2e** (113 mg, 78%). To the solution of this solid in dichloromethane (6 mL) tris(4-bromophenyl)aminium hexachloroantimonate (450 mg, 0.551 mmol) was added, and the solution was stirred at room temperature for 30 min under Ar. The resulting brown solid was filtered, washed with a small amount of dichloromethane, and dissolved in acetonitrile (1 mL). Zn (200 mg) was added to the solution and the mixture was heated at reflux for 1 min. After the addition of dichloromethane (20 mL), the mixture was filtered and evaporation of the solvent followed by separation with a short column (alumina/CH<sub>2</sub>Cl<sub>2</sub>) gave **1e** (42 mg, 29% based on the aldehyde) as a yellow solid.

*Synthesis of 1k*

A solution of BuLi in hexane (1.6 mol dm<sup>-3</sup>, 0.57 mL, 0.91 mmol) was added to a solution of phosphonate ester **4** (250 mg, 0.828 mmol) in dry THF (8 mL) at -70°C under Ar. The solution was stirred for 10 min, and 2,3-(methylenedioxy)benzaldehyde (83 mg, 0.553 mmol) was added to it. The mixture was stirred for a further 30 min at -70°C and allowed to warm to room temperature. To the solution water (30 mL) was added and the product was extracted with dichloromethane. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to give a brown oil **2k** which was used for a later reaction without further purification. The oil was dissolved in dichloromethane (8 mL) and aminium salt (500 mg, 0.613 mmol) was added. The solution was stirred at room temperature for 30 min under Ar. The same

work-up with the synthesis of **1e** afforded **1k** (115 mg, 64% based on the aldehyde) as a yellow solid.

The dication salts **1k**·(PF<sub>6</sub>)<sub>2</sub>·(H<sub>2</sub>O)<sub>4</sub> and **1l**·(PF<sub>6</sub>)<sub>2</sub> were obtained by electrochemical oxidation of **1** in the presence of Bu<sub>4</sub>NPF<sub>6</sub>. Single crystals of Cu complexes were obtained by diffusion method from a solution of **1** and CuCl<sub>2</sub> in acetonitrile using an H-tube.

*Crystal Structure Analysis*

Reflection data for **1a**·CuCl<sub>4</sub>, **1c**·CuCl<sub>4</sub>, **1e**·Cu<sub>2</sub>Cl<sub>6</sub> and **1k**·(PF<sub>6</sub>)<sub>2</sub>·(H<sub>2</sub>O)<sub>4</sub> were collected on an Enraf–Nonius CAD4 diffractometer using Cu Kα radiation (λ = 1.54178 Å) at 296 K, and reflection data for **1e**·Cu<sub>2</sub>Cl<sub>6</sub>·(H<sub>2</sub>O)<sub>0.22</sub>, **1g**·Cu<sub>2</sub>Cl<sub>6</sub> and **1l**·(PF<sub>6</sub>)<sub>2</sub> were collected on a Rigaku R-Axis IV imaging plate area detector with MoKα radiation (λ = 0.71070 Å) at 296 K. Absorption correction was applied to **1a**·CuCl<sub>4</sub>, **1c**·CuCl<sub>4</sub>, **1e**·Cu<sub>2</sub>Cl<sub>6</sub> and **1k**·(PF<sub>6</sub>)<sub>2</sub>·(H<sub>2</sub>O)<sub>4</sub> using empirical procedures based on azimuthal ψ scans of seven reflections having an Eulerian angle, χ, near 90°. All structures were solved by direct methods and refined by full-matrix least squares on F<sup>2</sup> with SHELX-97 (8). All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were placed in geometrically calculated positions and refined by using a riding model.

*Crystal Data for 1a·CuCl<sub>4</sub>*

C<sub>28</sub>H<sub>18</sub>Cl<sub>4</sub>CuS<sub>4</sub>, *M* = 688.00, dark green needle, monoclinic, space group *C2/c*, *a* = 18.1946(12) Å, *b* = 10.2518(5) Å, *c* = 16.4991(12) Å, β = 111.588(7)°, *V* = 2861.7(3) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.597 g cm<sup>-3</sup>, *F*(000) = 1388, μ = 7.386 mm<sup>-1</sup>, crystal dimensions 0.30 × 0.05 × 0.05 mm<sup>3</sup>, 3023 reflections collected, 2914 independent, *R*<sub>1</sub> = 0.0374, *wR*<sub>2</sub> = 0.0972 for *I* > 2σ(*I*), *R*<sub>1</sub> = 0.0838, *wR*<sub>2</sub> = 0.1231, *S* = 0.842 for all data.

*Crystal Data for 1c·CuCl<sub>4</sub>*

C<sub>28</sub>H<sub>16</sub>Cl<sub>6</sub>CuS<sub>4</sub>, *M* = 756.89, red plate, orthorhombic, space group *Pbcn*, *a* = 21.458(6) Å, *b* = 8.278(3) Å, *c* = 16.808(4) Å, *V* = 2986(2) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.684 g cm<sup>-3</sup>, *F*(000) = 1516, μ = 8.751 mm<sup>-1</sup>, crystal dimensions 0.30 × 0.05 × 0.02 mm<sup>3</sup>, 2349 reflections collected, 2027 independent, *R*<sub>1</sub> = 0.0721, *wR*<sub>2</sub> = 0.1283 for *I* > 2σ(*I*), *R*<sub>1</sub> = 0.3170, *wR*<sub>2</sub> = 0.2070, *S* = 0.864 for all data.

*Crystal Data for 1e·Cu<sub>2</sub>Cl<sub>6</sub>*

C<sub>30</sub>H<sub>16</sub>Cl<sub>6</sub>Cu<sub>2</sub>N<sub>2</sub>S<sub>4</sub>, *M* = 872.47, brown prism, triclinic, space group *P1̄*, *a* = 9.3709(6) Å, *b* = 10.5315(6) Å, *c* = 10.5612(7) Å, α = 62.083(5)°, β = 85.496(5)°, γ = 64.412(5)°, *V* = 820.60(9) Å<sup>3</sup>, *Z* = 1, *D*<sub>c</sub> = 1.766 g cm<sup>-3</sup>, *F*(000) = 434, μ = 8.690 mm<sup>-1</sup>, crystal dimensions 0.30 × 0.10 × 0.10 mm<sup>3</sup>,

3533 reflections collected, 3344 independent,  $R_1 = 0.0361$ ,  $wR_2 = 0.0944$  for  $I > 2\sigma(I)$ ,  $R_1 = 0.0465$ ,  $wR_2 = 0.1004$ ,  $S = 1.035$  for all data.

#### Crystal Data for **1e** · $\text{Cu}_2\text{Cl}_6 \cdot (\text{H}_2\text{O})_{0.22}$

$\text{C}_{30}\text{H}_{16}\text{Cl}_6\text{Cu}_2\text{N}_2\text{S}_4 \cdot (\text{H}_2\text{O})_{0.22}$ ,  $M = 876.43$ , brown prism, triclinic, space group  $P\bar{1}$ ,  $a = 9.585(2)$  Å,  $b = 11.536(3)$  Å,  $c = 9.309(5)$  Å,  $\alpha = 103.30(3)^\circ$ ,  $\beta = 107.87(3)^\circ$ ,  $\gamma = 109.04(2)^\circ$ ,  $V = 861.4(5)$  Å<sup>3</sup>,  $Z = 1$ ,  $D_c = 1.751$  g cm<sup>-3</sup>,  $F(000) = 454$ ,  $\mu = 1.975$  mm<sup>-1</sup>, crystal dimensions  $0.25 \times 0.10 \times 0.05$  mm<sup>3</sup>, 2695 reflections collected, 2695 independent,  $R_1 = 0.0788$ ,  $wR_2 = 0.2061$  for  $I > 2\sigma(I)$ ,  $R_1 = 0.0869$ ,  $wR_2 = 0.2214$ ,  $S = 0.912$  for all data.

#### Crystal Data for **1g** · $\text{Cu}_2\text{Cl}_6$

$\text{C}_{24}\text{H}_{14}\text{Cl}_6\text{Cu}_2\text{F}_4\text{S}_8$ ,  $M = 974.61$ , purple needle, monoclinic, space group  $P2_1/n$ ,  $a = 12.587(2)$  Å,  $b = 8.9306(14)$  Å,  $c = 14.774(7)$  Å,  $\beta = 92.40(2)^\circ$ ,  $V = 1659.3(9)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.951$  g cm<sup>-3</sup>,  $F(000) = 964$ ,  $\mu = 2.311$  mm<sup>-1</sup>, crystal dimensions  $0.30 \times 0.15 \times 0.10$  mm<sup>3</sup>, 2924 reflections collected, 2862 independent,  $R_1 = 0.0502$ ,  $wR_2 = 0.1212$  for  $I > 2\sigma(I)$ ,  $R_1 = 0.0587$ ,  $wR_2 = 0.1277$ ,  $S = 0.967$  for all data.

#### Crystal Data for **1k** · $(\text{PF}_6)_2 \cdot (\text{H}_2\text{O})_4$

$\text{C}_{26}\text{H}_{20}\text{F}_{12}\text{O}_8\text{P}_2\text{S}_8$ ,  $M = 1006.85$ , dark green needle, triclinic, space group  $P1\bar{1}$ ,  $a = 8.3330(11)$  Å,  $b = 8.861(2)$  Å,  $c = 14.962(3)$  Å,  $\alpha = 75.850(18)^\circ$ ,  $\beta = 74.700(13)^\circ$ ,  $\gamma = 71.504(18)^\circ$ ,  $V = 994.9(3)$  Å<sup>3</sup>,  $Z = 1$ ,  $D_c = 1.677$  g cm<sup>-3</sup>,  $F(000) = 504$ ,  $\mu = 5.858$  mm<sup>-1</sup>, crystal dimensions  $0.50 \times 0.05 \times 0.02$  mm<sup>3</sup>, 4344 reflections collected, 4053 independent,  $R_1 = 0.1070$ ,  $wR_2 = 0.2659$  for  $I > 2\sigma(I)$ ,  $R_1 = 0.2925$ ,  $wR_2 = 0.3698$ ,  $S = 0.961$  for all data.

TABLE 1  
Oxidation Potentials of Donors 1<sup>a</sup>

Donor	$R, R'$	$R_1$	$R_2$	$R_3$	$R_4$	$E/V$
<b>1a</b>	(CH=CH) <sub>2</sub>	H	H	H	H	0.61 (2e) <sup>b</sup>
<b>1b</b>	(CH=CH) <sub>2</sub>	F	H	H	F	0.66, 0.85 <sup>b</sup>
<b>1c</b>	(CH=CH) <sub>2</sub>	H	H	Cl	H	0.67 (2e) <sup>b</sup>
<b>1d</b>	(CH=CH) <sub>2</sub>	CN	H	H	H	0.61, 0.84
<b>1e</b>	(CH=CH) <sub>2</sub>	H	H	CN	H	0.64 (2e)
<b>1f</b>	(CH=CH) <sub>2</sub>	OCH <sub>2</sub> O	H	H	H	0.57, 0.70
<b>1g</b>	SCH <sub>2</sub> CH <sub>2</sub> S	F	H	H	F	0.51, 0.70 <sup>b</sup>
<b>1h</b>	SCH <sub>2</sub> CH <sub>2</sub> S	Cl	H	H	H	0.38, 0.60 <sup>b</sup>
<b>1i</b>	SCH <sub>2</sub> CH <sub>2</sub> S	CN	H	H	H	0.52, 0.70
<b>1j</b>	SCH <sub>2</sub> CH <sub>2</sub> S	H	H	CN	H	0.60 (2e)
<b>1k</b>	SCH <sub>2</sub> CH <sub>2</sub> S	OCH <sub>2</sub> O	H	H	H	0.39, 0.53
<b>1l</b>	H, H	F	H	H	F	0.42, 0.65 <sup>b</sup>

<sup>a</sup> 0.1 mol dm<sup>-3</sup> Bu<sub>4</sub>NPF<sub>6</sub> in PhCN, Pt electrode, scan rate 100 mV s<sup>-1</sup>,  $E/V$  vs SCE.

<sup>b</sup> Ref. (3a).

#### Crystal Data for **1l** · $(\text{PF}_6)_2$

$\text{C}_{20}\text{H}_{10}\text{F}_{16}\text{P}_2\text{S}_4$ ,  $M = 744.46$ , yellow needle, monoclinic, space group  $P2_1/c$ ,  $a = 6.0616(15)$  Å,  $b = 19.787(5)$  Å,  $c = 11.535(8)$  Å,  $\beta = 101.82(5)^\circ$ ,  $V = 1354(1)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.826$  g cm<sup>-3</sup>,  $F(000) = 736$ ,  $\mu = 0.592$  mm<sup>-1</sup>, crystal dimensions  $0.70 \times 0.15 \times 0.05$  mm<sup>3</sup>, 1909 reflections collected, 1903 independent,  $R_1 = 0.0575$ ,  $wR_2 = 0.1301$  for  $I > 2\sigma(I)$ ,  $R_1 = 0.0719$ ,  $wR_2 = 0.1396$ ,  $S = 1.002$  for all data.

## RESULTS AND DISCUSSION

Cyano and methylenedioxy derivatives were newly prepared in moderate yields using a chemical-oxidative

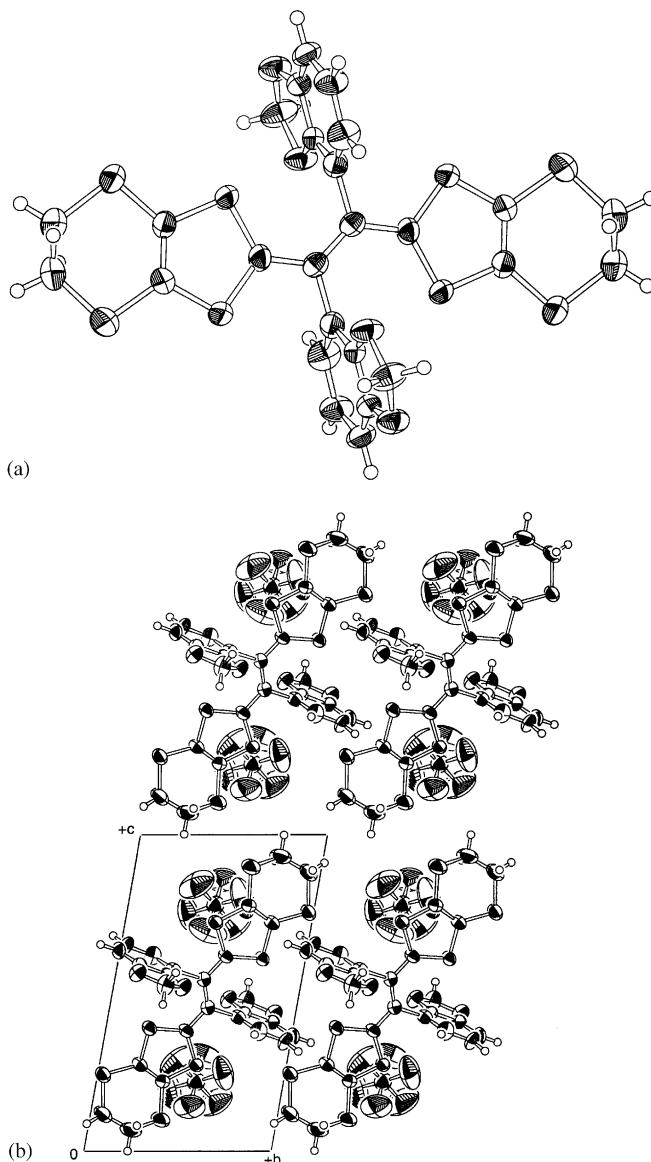


FIG. 1. (a) Molecular structure of dication of **1k**. (b) Crystal structure of **1k** ·  $\text{PF}_6 \cdot (\text{H}_2\text{O})_4$  viewed along the  $a$ -axis. Water molecules are omitted for clarity.

**TABLE 2**  
**Dihedral Angles and Intermolecular Distances in Dication Salts**

Salt	Dihedral angle <sup>a</sup> (deg)	Distance <sup>b</sup> (Å)
<b>1a</b> · CuCl <sub>4</sub>	81.2	3.86 and 5.21 <sup>c</sup>
<b>1c</b> · CuCl <sub>4</sub>	79.7	— <sup>d</sup>
<b>1e</b> · Cu <sub>2</sub> Cl <sub>6</sub>	79.6	3.47 <sup>c</sup>
<b>1e</b> · Cu <sub>2</sub> Cl <sub>6</sub> · (H <sub>2</sub> O) <sub>0.22</sub>	85.8	3.87 <sup>c</sup>
<b>1g</b> · Cu <sub>2</sub> Cl <sub>6</sub>	86.1	— <sup>d</sup>
<b>1k</b> · (PF <sub>6</sub> ) <sub>2</sub> · (H <sub>2</sub> O) <sub>4</sub>	84.5	7.78 <sup>e</sup>
<b>1l</b> · (PF <sub>6</sub> ) <sub>2</sub>	86.6	4.61 <sup>e</sup>

<sup>a</sup> Between 1,3-dithiole and phenyl groups.

<sup>b</sup> Between 1,3-dithiole groups.

<sup>c</sup> Two-dimensional stacking.

<sup>d</sup> Mixed stacking.

<sup>e</sup> One-dimensional stacking.

coupling of the corresponding 1,4-dithiafulvenes. This result indicates that this synthetic method can be applied to the synthesis of TTF vinylogues **1** regardless of the substituents on the phenyl groups.

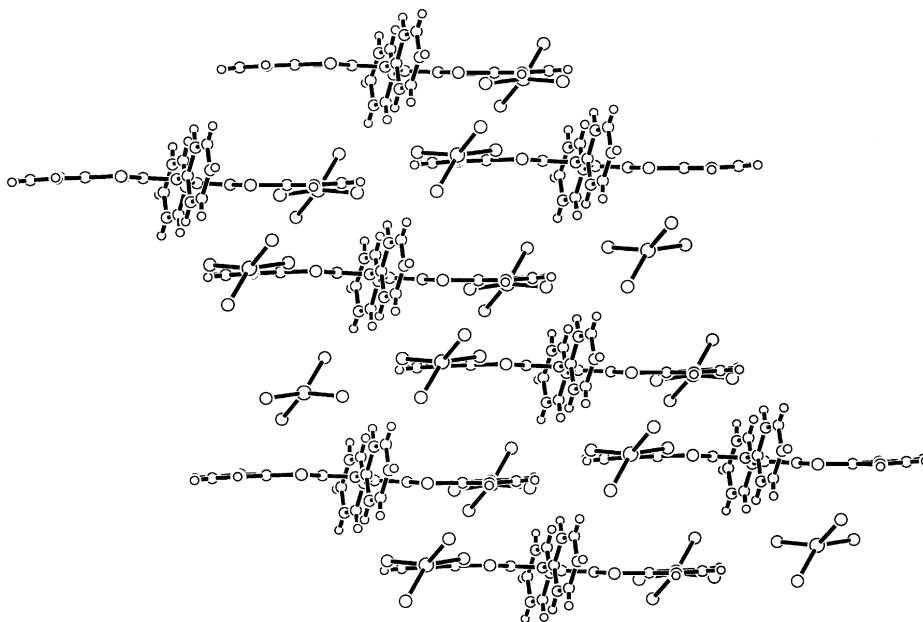
The oxidation potentials measured by cyclic voltammetry are summarized in Table 1. The values are positively shifted by introducing electron-withdrawing substituents such as cyano and negatively shifted by electron-donating ones such as methylenedioxy. The parent compound **1l** exhibits lower oxidation potentials than the corresponding dibenzo one **1b** and bisethylenedithio one **1g**, indicating that the parent one is the strongest donor among them. As pointed out previously, the *ortho*-substituted derivatives show reversible two-stage one-electron oxidation waves, while the *para*-substituted ones as well as non-substituted

phenyl derivative **1a** show one-stage two-electron waves. This fact can be explained by considering that the *ortho*-substituents increase the steric interactions and favor the geometry with the phenyl groups twisted, where the cation radicals can be stabilized by delocalization of the electron. On the other hand, the cation radicals of the *para*-substituted derivatives are unstable and become dication by further oxidation.

We have obtained the cation radical salts of *ortho*-substituted derivatives such as **1b** and **1g** by electrochemical oxidation (3a, 4–6). When donors **1k** and **1l** were electrochemically oxidized under the same conditions, however, the dication salts were obtained instead of the cation radical salts although the donors show two-step one-electron oxidation. This result may be explained by considering that they are more easily oxidized due to their lower oxidation potentials compared with the other donors.

The molecular structure of dication of **1k** is shown in Fig. 1a, which is similar to those of the cation radicals of **1**. The TTF vinylogue skeleton is planar and the 1,3-benzodioxole moieties are almost orthogonal to it with the dihedral angles of 84.5° between 1,3-benzodioxole moieties and the 1,3-dithioles. The crystal structure of **1k** · (PF<sub>6</sub>)<sub>2</sub> · (H<sub>2</sub>O)<sub>4</sub> is shown in Fig. 1b. The dication **1k** is stacked in a one-dimensional fashion along the *a*-axis. The PF<sub>6</sub> anions are sandwiched between the two 1,3-dithiole rings.

The molecular structure of dication of **1l** is similar to that of **1k**, where the dihedral angle between the phenyl groups and the 1,3-dithioles is 86.6°. This fact indicates



**FIG. 2.** Two-dimensional  $\pi$ -overlapping of **1a** · CuCl<sub>4</sub>.

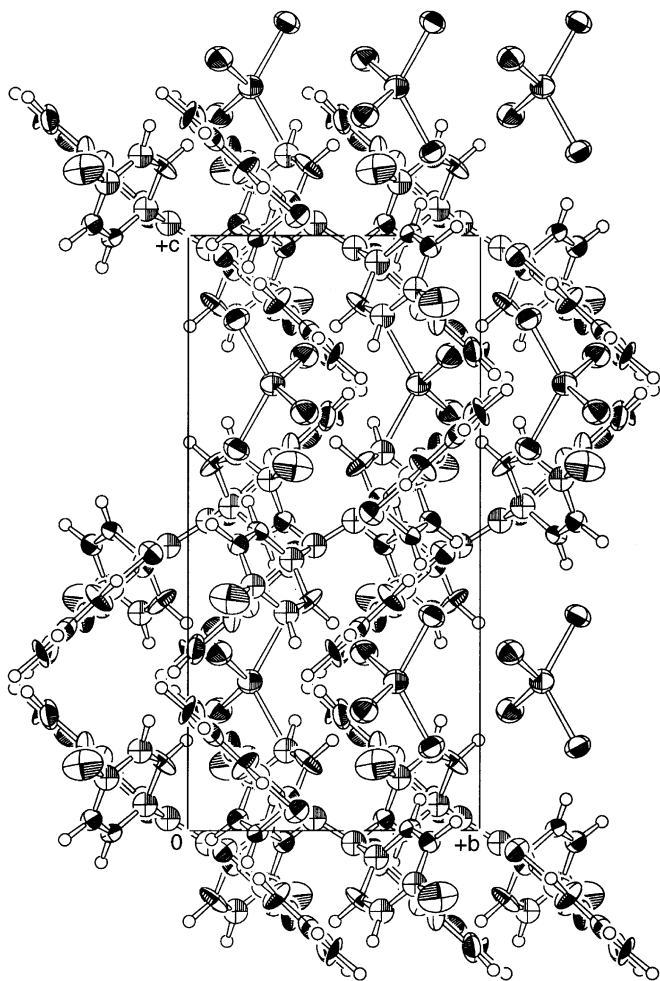


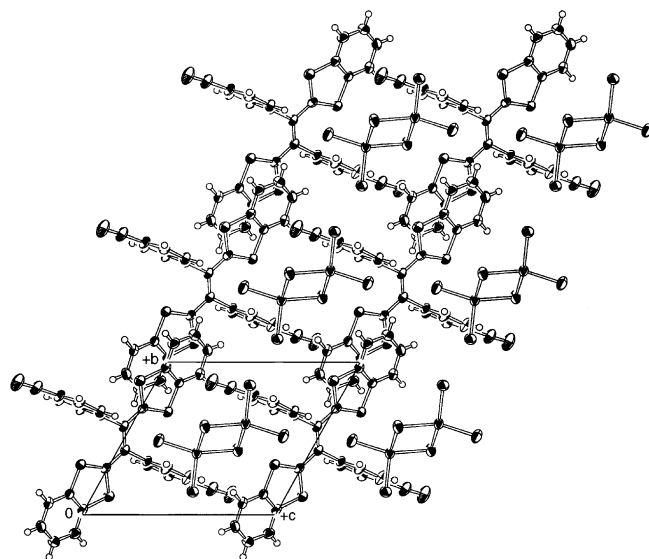
FIG. 3. Crystal structure of  $1c \cdot CuCl_4$  viewed along the  $a$ -axis.

that the dications as well as the cation radicals of **1** with *ortho*-substituted phenyl groups have a geometry of planar TTF vinylogue skeleton in contrast to the non-planar structure of the neutral molecule of **1** (3). Dication **II** also forms a one-dimensional stacking. The  $PF_6$  anions, however, are located between the stacks. The intermolecular distance between the 1,3-dithiole groups in the **II** salt is shorter than that in the **Ik** salt as shown in Table 2. This is attributed to the reduced steric interactions caused by the phenyl substituents.

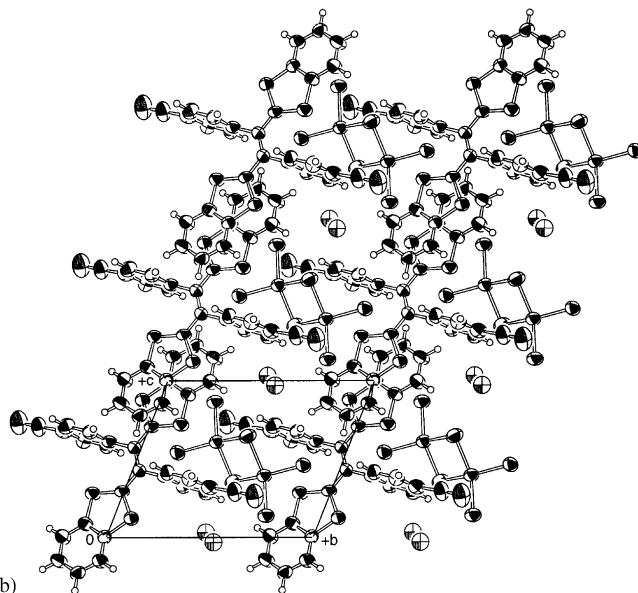
The TTF vinylogues **1a** and **1c** which undergo one-stage two-electron oxidation afforded dication salts  $1a \cdot CuCl_4$  and  $1c \cdot CuCl_4$  in the reaction with anhydrous  $CuCl_2$ . The molecular structures of the dications are similar to those of the dications of **Ik** and **II**. The dihedral angles between the 1,3-dithiole and phenyl groups are summarized in Table 2. This fact indicates that the dications of **1** whose cation radicals are considered to be unstable probably due to the non-planar structures also have a geometry with a planar TTF vinylogue skeleton. In the crystal structure of

$1a \cdot CuCl_4$ , the benzo-1,3-dithiole parts are overlapped in a manner of bridging two molecules to make a unique infinite  $\pi$ -stacking as shown in Fig. 2. The Cu ions are included in a mixed stacking way. On the other hand, in  $1c \cdot CuCl_4$  direct overlapping between the donor molecules is not observed, but a mixed stacking affords columns which are developed in two directions as shown in Fig. 3.

Cyano-containing molecules **1e** afforded a complex  $1e \cdot Cu_2Cl_6$  in the reaction with anhydrous  $CuCl_2$ . The cyano groups were expected to coordinate to the Cu atom. However, such coordination was not observed; instead, the similar network of the donor molecules as that of  $1b \cdot PF_6$



(a)



(b)

FIG. 4. Crystal structure of (a)  $1e \cdot Cu_2Cl_6$  and (b)  $1e \cdot Cu_2Cl_6 \cdot (H_2O)_{0.22}$  viewed along the  $a$ -axis.

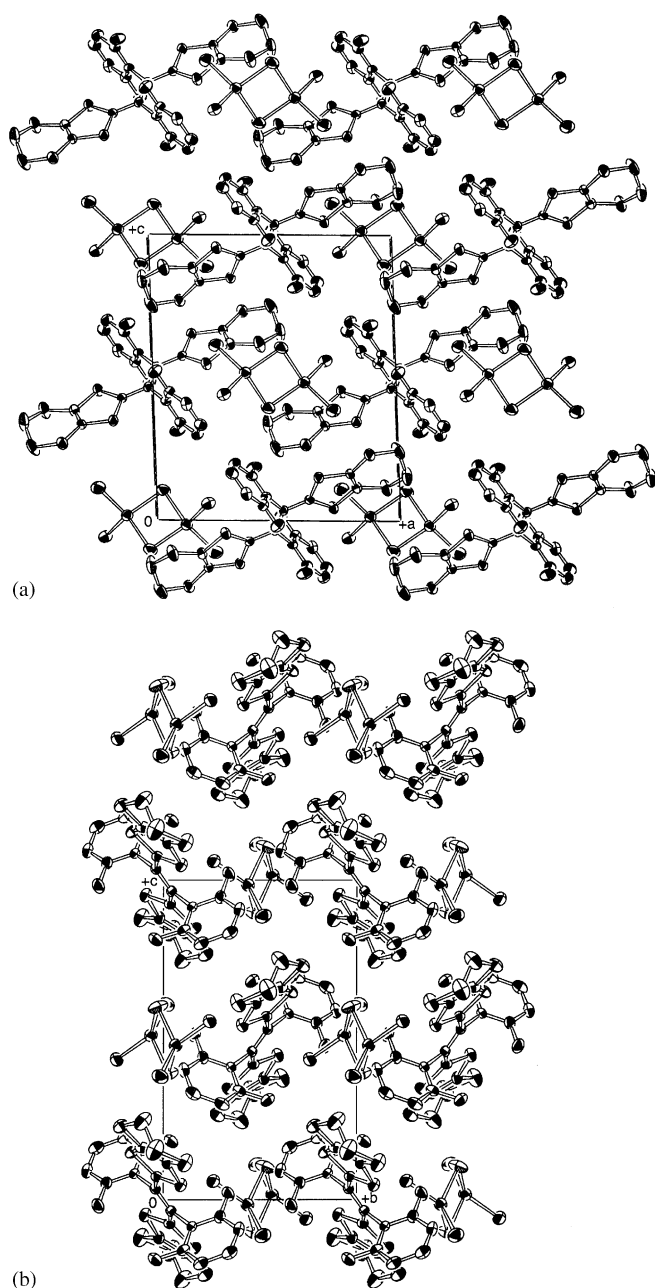


FIG. 5. Crystal structure of  $1g \cdot Cu_2Cl_6$  viewed along the (a)  $b$ -axis and (b)  $a$ -axis.

or  $1a \cdot CuCl_4$  involving two-dimensional  $\pi-\pi$  overlapping between the donor molecules was observed as shown in Fig. 4a. The formation of  $Cu_2Cl_6$  is explained by dimerization of unstable monovalent Cu species (9). Interestingly, when  $CuCl_2$  dihydrate was used, a different crystal structure,  $1e \cdot Cu_2Cl_6 \cdot (H_2O)_{0.22}$  was formed, where the arrangement of the  $Cu_2Cl_6$  is different and water molecules are involved although the network of the donor molecules

is the same as shown in Fig. 4b. The intermolecular distance is a little larger in the water containing salt as shown in Table 2.

Bisethylenedithio derivative  $1g$  affords a stable cation radical salt upon electrochemical oxidation (5). However, the reaction of  $1g$  with  $CuCl_2$  gave the dication salt with  $Cu_2Cl_6$ . The crystal structure of  $1g \cdot Cu_2Cl_6$  is shown in Fig. 5. A similar mixed stacking as that of  $1c \cdot CuCl_4$  was observed.

In conclusion, we have succeeded in preparing dication salts of novel TTF vinyllogues with unusual crystal structures. Studies on the physical properties of the dication salts are now in progress.

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