Cation Radical Salts of Bis(2,5-dimethylthieno)tetratellurafulvalene: Electrical Conductivities and a Crystal Structure

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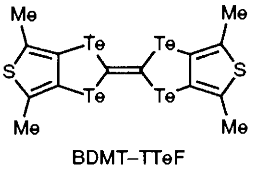
Highly conducting cation radical salts of 2,5-dimethylthiophene-fused tetratellurafulvalene (BDMT-TTeF) have been prepared and the crystal structure of the perchlorate salt has been determined.

The tellurium analogues of tetrathiafulvalene (TTF) derivatives are quite important to line up the sulfur, selenium and tellurium series, and thereby, to study the stepwise changes of the electronic properties and the critical structural and electronic-function relationships in organic conductors and superconductors. To date, however, the only known tetratellurafulvalene (TTeF) derivatives are hexamethylene-TTeF (HMTTeF),[1] dibenzo-TTeF (DBTTeF),[2] bis(dimethylthieno)-TTeF (BDMT-TTeF)[3] and the parent TTeF itself which has most recently been prepared.[4] Much less information is available on their cation radical salts[5,6] and their crystal structures.[7] BDMT-TTeF was prepared first by Lerstrup *et al.*[5] Among its cation radical salts only the AsF_6 salt has been known to show a high conductivity (*ca.* 50 S cm^{-1}).[5] We report here the highly conducting perchlorate salt of BDMT-TTeF, along with several other salts, and its crystal structure as determined by single-crystal X-ray diffraction. We believe this is the first structural report concerned with the cation radical salts of BDMT-TTeF and thiophene-fused TTF analogues.[5,8]



BDMT–TTeF

tion of BDMT-TTeF under a constant current (1 μA) in the presence of Bu^n_4NX as supporting electrolyte with 1,1,2-trichloroethane as solvent. The inorganic counter anions X are ClO_4, ReO_4, AsF_6, PF_6 and SbF_6. In each case, black needles of *ca.* 0.5 × 0.15 × 0.06 nm crystallized within a week. The stoichiometries of $(BDMT\text{-}TTeF)_3(AsF_6)_2$ and $(BDMT\text{-}TTeF)_3(PF_6)_2$ were determined on the basis of the XPS peak intensities of F 1s and S 2p electrons. Electrical conductivities of the radical salts, measured with the standard d.c. current and four-probe method, are fairly high (Table 1), being almost 100 times higher than those observed in the radical salts of the corresponding selenium (BDMT-TSF) and sulfur (BDMT-TTF) donors.[5] The temperature dependence of conductivities shows a semiconducting behaviour with fairly small activation energy for each salt (Table 1).

A crystal structure of the perchlorate salt has been

Table 1 Conductivity and activation energy of the radical cation salts of BDMT–TTeF

Anion	Conductivity σ/S cm^{-1}	Activation energy E_a/eV
ClO_4	2.6	0.07
ReO_4	0.92	0.17
AsF_6	76	0.09
PF_6	25	0.18
SbF_6	0.17	0.16

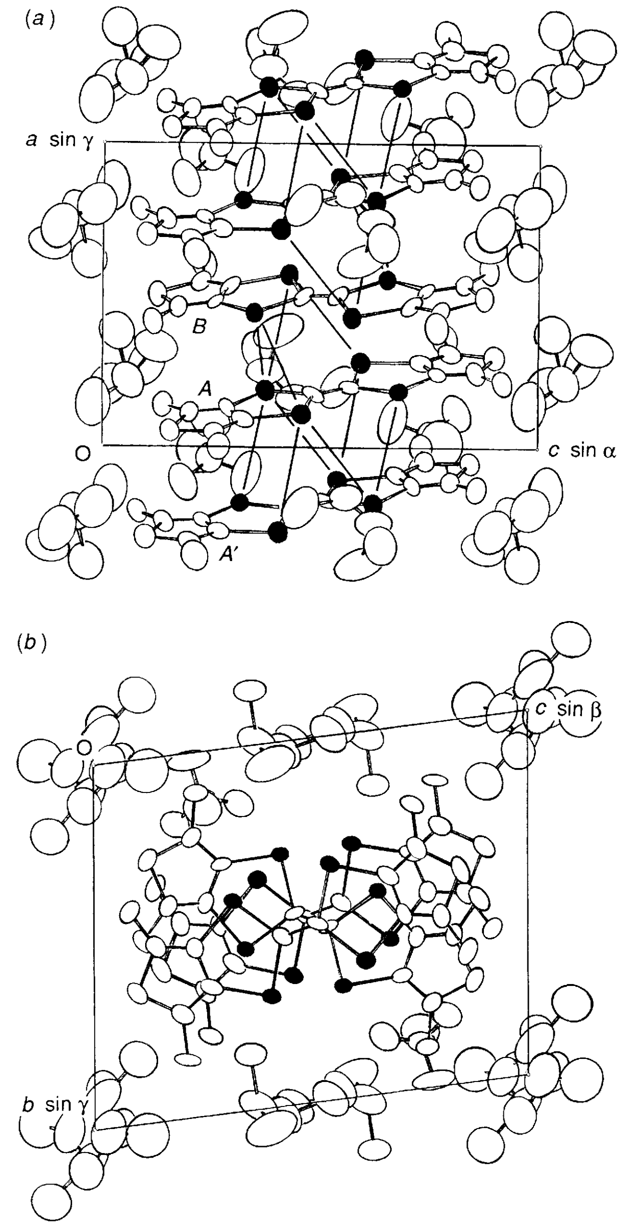


Fig. 1 Crystal structure of (BDMT–TTeF)$_3$(ClO$_4$)$_2$(C$_2$H$_3$Cl$_3$)$_4$, viewed along the *b* axis (*a*) and along the *a* axis (*b*). The bold lines show Te···Te contacts that are shorter than the expected van der Waals separation. Three chlorine atoms are placed on C-1 of the disordered 1,1,2-trichloroethane molecules.

determined by X-ray diffraction.† The crystal includes solvent molecules and is composed of 3:2:4 stoichiometry of BDMT-TTeF, ClO$_4$ and C$_2$H$_3$Cl$_3$. The molecular packing is illustrated in Fig. 1. The dichloromethyl groups of two of 1,1,2-trichloroethane molecules in the unit cell are orientationally disordered. The BDMT-TTeF molecules are essentially planar with small amount of puckering at the tellurium atoms. This is the most characteristic feature in contrast to the solid-state structure of uncomplexed BDMT–TTeF, which has been shown to adopt a dimeric structure with a highly distorted asymmetric boat conformation.[3] Thus, the dihedral angle between the tetratelluraethylene core and the exterior dimethylthienoditellurole planes is dramatically changed from 47.1° in the neutral state to almost 0° in the cation radical salt. The C–Te–C angles (av. 92.9°) are expanded by 1.8 and 1.3° as compard with the neutral molecule[4] of BDMT-TTeF, whereas the central C=C bond (av. 1.315 Å) is shorter than that in uncomplexed BDMT-TTeF (1.331 Å).[3] These results would be ascribable to the dramatic conformational change from the bent to the planar one according to complexation.

The unit cell contains three BDMT-TTeF molecules [the molecules **A**, **B** and **A′** in Fig. 1(*a*)] which make a trimeric molecular column along the *a* axis. An inversion centre is present at the centre of molecule B and there are two types of overlapping with intermolecular spacings of 3.54 Å between A and B, and 3.80 Å between A and A′. The mode of the molecular stacking in the column is quite different from those found so far in other TTF derivatives and analogues. Molecules **A** and **A′** are twisted to B by approximately 45° [Fig. 1(*b*)]. Thus, the molecular overlapping is not in sliding zigzag motif but in twisted fashion. This would be explained in terms of steric interactions between the methyl groups and the tellurium atoms: such interactions would be effectively avoided by twisting the molecular axis rather than parallel sliding.

The stacking columns are separated from each other by anionic ClO$_4$ species and solvent C$_2$H$_3$Cl$_3$ molecules, so that no significant short contacts are observed between the stacking columns: the shortest intercolumnar S···S distance is 4.12 Å. The perchlorate salt is, therefore, regarded to be a highly one-dimensional conductor. On the other hand, there are 14 intermolecular short contacts in the stacks ranging from 3.93 to 4.28 Å, which are shorter than twice the van der Waals radius of the tellurium atom (2.20 Å). These contacts as well as high polarizability of tellurium atoms, which reduces on-site Coulombic repulsion, would be responsible for the high conductivity of the perchlorate salt.

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† *Crystal data* for (BDMT–TTeF)$_3$(ClO$_4$)$_2$(C$_2$H$_3$Cl$_3$)$_4$: C$_{50}$H$_{48}$Cl$_{14}$O$_8$S$_6$Te$_{12}$, M = 2730.39, triclinic, space group $P\bar{1}$, a = 11.048(2), b = 12.983(5), c = 15.097(4) Å, α = 97.43(1), β = 91.93(1), γ = 74.99(1)°, V = 2073.9(18) Å^3, $F(000)$ = 1370, Z = 1, D_c = 2.41 g cm^{-3}. A total of 4439 reflections within 2θ = 55 was collected using graphite-monochromated Mo-Kα radiation. Final R = 0.052 and R_w = 0.056 for 3645 reflections with $F_o > 3\sigma$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors Issue No. 1.