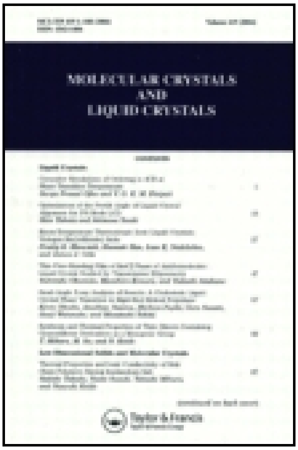

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New $(TMTSF)_2X$ Derivatives: A Change in the Selenium Network Dimensionality Derived From the Molecular and Crystal Structures of $(TMTSF)_2(Fso_3)$ [T=298K, 123K] and $(TMTSF)_2(Bro_4)$ T=298K

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NEW $(TMTSF)_2X$ DERIVATIVES: A CHANGE IN THE SELENIUM NETWORK DIMENSIONALITY DERIVED FROM THE MOLECULAR AND CRYSTAL STRUCTURES OF $(TMTSF)_2(FSO_3)$ [T=298K, 123K] AND $(TMTSF)_2(BrO_4)$ T=298K

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We report the first crystallographic analysis, as a function of temperature, of a TMTSF derivative. Both $(TMTSF)_2$-(FSO_3) and $(TMTSF)_2(BrO_4)$ are isostructural (triclinic, with space group $P\bar{1}$) with superconducting $(TMTSF)_2(ClO_4)$. $(TMTSF)_2(FSO_3)$ undergoes a metal-to-insulator transition at 86-90K as observed by microwave conductivity, D.C. conductivity, and magnetic susceptibility. The crystal structure contains 2-dimensional sheets of short Se-Se contacts in the molecular stacking direction and perpendicular to the stacking direction. The temperature

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dependent variations in these contact distances appear to be of special importance in determining the conduction properties of these materials, and are observed to change in a surprising manner when $(TMTSF)_2(FSO_3)$ is cooled (298 → 123K). The homoatomic Se separations within each TMTSF molecule appear to increase slightly, but not significantly. At the same time the entire 2-dimensional sheet of intermolecular (*intra*- and *inter*stack) Se-Se contacts between TMTSF molecules contract quite anisotropically, which results in an increase in "dimensionality" of the Se-Se network. Hence, an increase in electrical conduction, in the absence of insulating phenomena, over the temperature range 298 → 123K is not surprising. The intermolecular Se-Se contact distances in $(TMTSF)_2(BrO_4)$ are significantly longer than in $(TMTSF)_2(FSO_3)$ which suggests that the room temperature electrical conductivity of the $(BrO_4)^-$ salt may be diminished compared to the $(FSO_3)^-$ analogue.

INTRODUCTION

The temperature dependence of the crystal structure of a TMTSF (bis-tetramethyltetraselenafulvalene) derivative, $(TMTSF)_2$-(FSO_3), and the synthesis and crystal structure determination of a novel perbromate derivative, $(TMTSF)_2(BrO_4)$, are reported. All $(TMTSF)_2X$ structures reported to date contain nearly planar TMTSF groups, which stack in columns extending along the high conductivity a axis of the unit cell of the triclinic space group $P\bar{1}$.[1,2] The TMTSF molecules also form infinite 2-dimensional molecular sheets, which lie perpendicular to a and extend in the a-b plane, thereby providing added "dimensionality" to the system beyond that provided solely by the 1-D molecular stacking of TMTSF moieties. However, the TMTSF molecules do not themselves form a 3-dimensional network because the sheets are separated along *c* by anions (X) which always appear to be in crystallographic disorder.

EXPERIMENTAL

Single crystals of $(TMTSF)_2(FSO_3)$ and $(TMTSF)_2(BrO_4)$ were obtained by electrochemical oxidation of neutral TMTSF in Cl_2CHCH_2Cl[6] using $n\text{-}Bu_4N(FSO_3)$ and $n\text{-}Bu_4N(BrO_4)$, respectively, as the supporting electrolytes. Perbromic acid, $HBrO_4$, the bromine analogue of $HClO_4$, was synthesized using a published procedure[3] and then $n\text{-}Bu_4N(BrO_4)$ salt was prepared by neutralization of the acid with a solution of $n\text{-}Bu_4NOH$.

The x-ray structural studies reported here were performed using MoK_α (λ = 0.71073 Å) radiation, and pertinent crystal data for $(TMTSF)_2(FSO_3)$ and $(TMTSF)_2(BrO_4)$, are given in Table 1.

RESULTS AND DISCUSSION

The most interesting result of our study of the crystal structure of a $(TMTSF)_2X$ salt, as a function of reduced temperature, was the observation of a surprising anisotropic shortening of the intermolecular (inter- and intrachain) Se-Se contacts that (we believe) indicates an increase in the "dimensionality" in the Se-Se network at low temperature (*vide infra*). This could, for example, correspond to the "dimensionality crossover"[4] (1-D to 2- or 3-D) observed in the variable-temperature polarized reflectance measurements of $(TMTSF)_2PF_6$. From Figure 1 we see no unusual structural changes upon cooling in the TMTSF molecule. The *intra*- and *inter*molecular Se-Se contacts are

TABLE 1 Crystal Data for $(TMTSF)_2X$ Derivatives

$(TMTSF)_2(FSO_3)$

$\underline{a}$ = 7.255(1), $\underline{b}$ = 7.680(1), $\underline{c}$ = 13.313(2), V_c = 695.3(2)
α = 84.40(1), β = 86.68(1), γ = 70.42(1) at T = 298K

2271 independent data, 1747 with $F^2 > 3\sigma(F^2)$
$4.0° \leq 2\theta \leq 50.0°$, u_c = 105.1 cm^{-1}, $R(F^2 > \sigma F^2)$ = 0.056

$\underline{a}$ = 7.150(1), $\underline{b}$ = 7.683(2), $\underline{c}$ = 13.227(2), V_c = 677.7(3)
α = 84.75(2), β = 87.43(2), γ = 69.52(2) at T = 123K

1600 independent data, 988 with $F^2 > 3\sigma(F^2)$
$4.0° \leq 2\theta \leq 35.0°$, u_c = 107.8 cm^{-1}, $R(F^2 > \sigma F^2)$ = 0.083

$(TMTSF)_2(BrO_4)$

$\underline{a}$ = 7.282(1), $\underline{b}$ = 7.714(2), $\underline{c}$ = 13.425(4), V_c = 707.2(3)
α = 83.74(2), β = 86.18(2), γ = 70.71(2) at T = 298K

1744 independent data, 1309 with $F^2 > 3\sigma(F^2)$
$4.0° \leq 2\theta \leq 45.0°$, u_c = 116.6 cm^{-1}, $R(F^2 > \sigma F^2)$ = 0.049

$\underline{a}$ = 7.180(1), $\underline{b}$ = 7.722(2), $\underline{c}$ = 13.341(3), V_c = 689.8(3)
α = 84.08(2), β = 87.26(2), γ = 69.63(1) at T = 125K

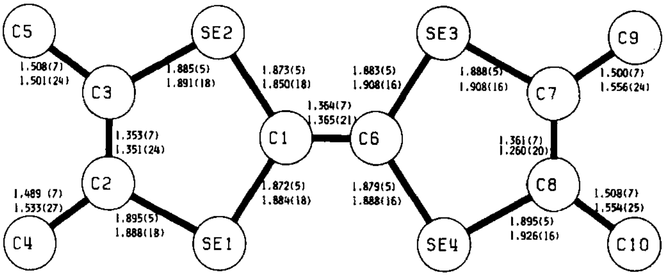

FIGURE 1 Bond distances in the TMTSF molecule at 298K (top) and 123K

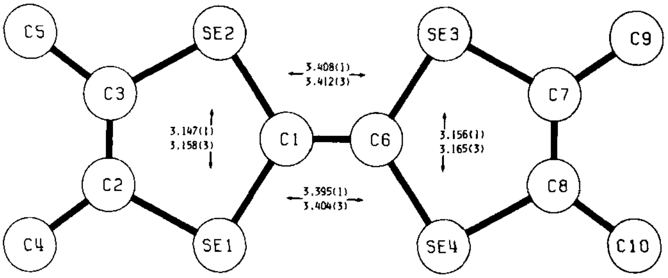

FIGURE 2 Intramolecular Se-Se distances in the TMTSF molecule at 298K (top) and 123K

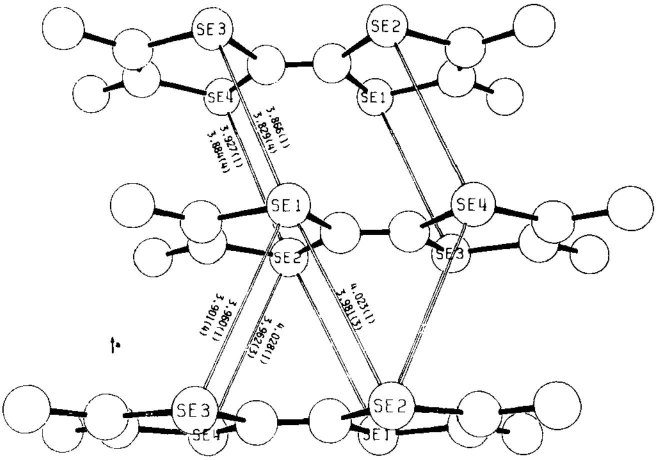

FIGURE 3 The intrastack Se-Se distances in $(TMTSF)_2(FSO_3)$ at 298K (top) and 123K

presented in Figures 2 and 3, respectively. The 2-dimensional Se-Se "sheet network" (Se-Se distances to 4.05 Å) is shown in Figure 4. These homoatomic Se distances appear to be insignificantly larger within the TMTSF molecule (Figure 2) while a considerable shortening in the intrastack Se-Se distances upon cooling, which indicates the "dimerization" in the lattice stack, is obvious (Figure 3). A comparison of intermolecular intrastack homoatomic Se contact distances in

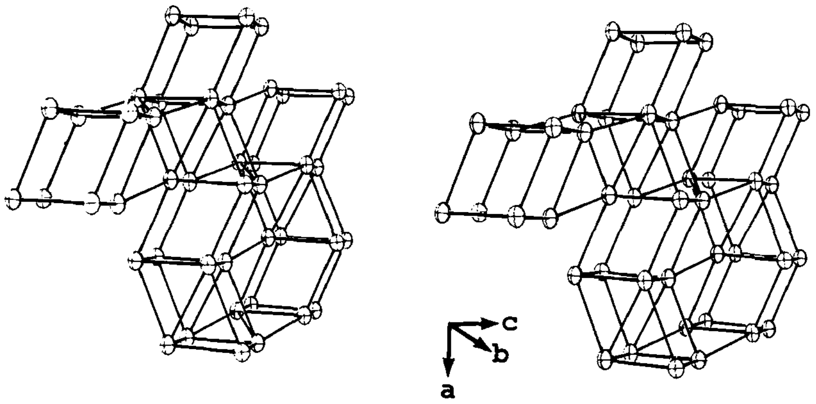

FIGURE 4 A stereoview of the Se-Se "sheet network" (Se-Se distances to 4.05 Å) in $(TMTSF)_2(FSO_3)$

TABLE 2 Intramolecular Se-Se Contacts to 5.0 Å for $(TMTSF)_2X$ Derivatives

	Distance (Å)				Distance (Å)		Distance (Å)	
Contact	$X=(FSO_3)^-$ T=298K	$X=(FSO_3)^-$ T=123K	ΔÅ	Δ/σ	$X=(BrO_4)^-$ T=298K	ΔÅ[a]	$X=(ClO_4)^-$ T=298K	ΔÅ[b]
Se1-Se2	3.147(1)	3.158(3)	0.011(3)	3.7	3.148(1)	0.001(1)	3.150(2)	0.003(2)
Se1-Se4	3.395(1)	3.404(3)	0.009(3)	3.0	3.392(1)	-0.003(1)	3.396(2)	0.001(2)
Se1-Se3	4.638(1)	4.650(2)	0.012(2)	6.0	4.635(1)	-0.003(1)	4.638(2)	0.000(2)
Se2-Se3	3.408(1)	3.412(3)	0.004(3)	1.3	3.412(1)	0.004(1)	3.405(2)	-0.003(2)
Se2-Se4	4.636(1)	4.647(2)	0.011(2)	5.5	4.638(1)	0.002(1)	4.638(2)	0.002(2)
Se3-Se4	3.156(1)	3.165(3)	0.009(3)	3.0	3.152(1)	-0.004(1)	3.158(2)	0.002(2)

[a] Δ = distance of $(BrO_4)^-$ — $(FSO_3)^-$(298K)

[b] Δ = distance of $(ClO_4)^-$ — $(FSO_3)^-$(298K)

$(TMTSF)_2X$ [X = $(FSO_3)^-$ (298K and 123K), $(BrO_4)^-$ and $(ClO_4)^-$] is presented in Table 2. The largest changes upon cooling involve the intermolecular interstack Se-Se separations (see Table 3). Detailed consideration of Table 3 reveals that the three intermolecular interstack Se-Se distances decrease by

TABLE 3 Intermolecular Se-Se Contacts to 5.0 Å for $(TMTSF)_2X$ Derivatives

Contact	Symmetry Operation	Distance (Å) $X=(FSO_3)^-$ (298K)	Distance (Å) $X=(FSO_3)^-$ (123K)	ΔÅ	Δ/σ	Distance (Å) $X=(BrO_4)^-$ (298K)	ΔÅ[a]	Δ/σ	Distance (Å) $X=(ClO_4)^-$ (298K)
Se1-Se3	i	3.866(1)	3.829(4)	-0.037(4)	- 9[b]	3.875(1)	0.009(1)	9	3.871(1)
Se1-Se4	ii	3.868(1)	3.782(2)	-0.086(2)	-43[c]	3.912(1)	0.044(1)	44	3.865(1)
Se1-Se2	iii	4.023(1)	3.981(3)	-0.042(3)	-14[b]	4.032(1)	0.009(1)	9	4.031(1)
Se1-Se3	iii	4.028(1)	3.962(3)	-0.066(3)	-22[b]	4.051(1)	0.023(1)	23	4.033(1)
Se1-Se2	i	4.120(1)	4.083(3)	-0.037(3)	-12	4.131(1)	0.011(1)	11	4.121(1)
Se2-Se2	iv	3.782(1)	3.684(4)	-0.098(4)	-25[c]	3.841(1)	0.059(1)	59	3.778(2)
Se2-Se4	i	3.927(1)	3.884(4)	-0.043(4)	-11[b]	3.931(1)	0.004(1)	4	3.934(1)
Se2-Se4	iii	3.960(1)	3.901(4)	-0.059(4)	-15[b]	3.981(1)	0.019(1)	19	3.964(1)
Se2-Se4	v	4.188(1)	4.225(2)	+0.037(2)	+19	4.178(1)	-0.010(1)	-10	4.192(2)
Se2-Se3	i	4.982(1)	4.962(3)	-0.020(3)	- 7	4.978(1)	-0.004(1)	- 4	4.985(2)
Se4-Se4	ii	3.952(1)	3.871(4)	-0.081(4)	-20[c]	3.946(1)	-0.006(1)	- 6	3.955(2)

[a] Δ = distance of $(BrO_4)^-$ — $(FSO_3)^-$(298K)

[b] Intermolecular intrastack Se-Se contact

[c] Intermolecular interstack Se-Se contact

Symmetry Operations
(i) 2-x 1-y 1-z
(ii) 1-x 2-y 1-z
(iii) 1-x 1-y 1-z
(iv) 2-x -y 1-z
(v) x y-1 z

20-43 Δ/σ while the five similar intrastack contacts contract by 9-22 Δ/σ.[7] We have eliminated from consideration the Se-Se distances of 4.255 Å and 4.962 Å, respectively, which greatly exceed both the van der Waals radius sum of 4.0 Å given by Pauling and 3.8 Å (Bondi). Obviously, short Se-Se separations do not necessarily require increased orbital overlap[5] and calculations of the total effect of the contractions in homoatomic Se separations in the sheet network in $(TMTSF)_2(FSO_3)$, shown in Figure 4, would be invaluable. Clearly, the various isostructural $(TMTSF)_2X$ derivatives which have been reported to date, some of which are superconducting, semiconducting, and insulating, provide a fertile field for low temperature structure-conductivity investigations.

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7. It should be noted that the shortest intermolecular Se-Se distances in both the FSO_3^- and ClO_4^- salts involve *inter*- and not *intra*stack Se-Se contacts.