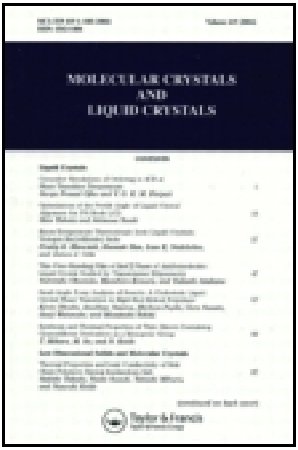

Molecular Crystals and Liquid Crystals

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Synthesis and Study of Electrochemically Grown Salts of Organic II-Donors

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SYNTHESIS AND STUDY OF ELECTROCHEMICALLY GROWN SALTS OF ORGANIC Π-DONORS*

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The effects of purity and crystal perfection on the properties of $(TMTSF)_2ClO_4$ are examined via SEM's and transition temperatures. Careful electrochemical techniques using gradient sublimed TMTSF starting material and short term oxidation result in high quality crystals. Preliminary work on HMTSF salts of PF_6^- and AsF_6^- is also reported.

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In studying the properties of conducting and superconducting organic salts, high quality single-crystal samples are necessary for meaningful experiments. In particular, the presence of impurities and crystal imperfections can significantly affect the behavior of most superconductors. We are concerned with the effects of purity and crystal perfection on the electrical and magnetic properties of the zero pressure organic superconductor, $(TMTSF)_2ClO_4$. Our results elsewhere describe $(TMTSF)_2ClO_4$ as a filamentary or layered superconductor near its T_c, 1.0 K, and as an anisotropic 3-D superconductor at lower temperatures.[1] Differences in sample purity and crystal quality were determined by their transition temperatures and SEM's. Preliminary work on two HMTSF salts is also reported.

Samples of $(TMTSF)_2ClO_4$ were grown electrochemically under constant current conditions using a method similar to the one described by Bechgaard, et al.[2] Crystals were obtained upon anodic oxidation of TMTSF (10^{-3} M) in 1,1,2-trichloroethane containing 5.11 X 10^{-3} M of $n\text{-}Bu_4NClO_4$. The current density was maintained at 1.6 μamps/cm using platinum electrodes. (Figure 1)

Experimental modifications included: (a) using unsublimed, once and twice gradient sublimed neutral TMTSF, and (b) varying the duration of the oxidation process.

We have found that the T_c values obtained from 4-probe resistance measurements on $(TMTSF)_2ClO_4$ samples show some correlation to the purity of the starting material, see Table 1. Resistance measurements were performed in a dilution refrigerator. The unsublimed TMTSF yielded crystals consistently having the lowest T_c values, 0.8 - 0.82 K, where T_c is defined as the midpoint of the broad resistivity transition. In the case of the once and twice sublimed materials, the T_c values were reasonably close although T_c for the twice sublimed sample was slightly lower (2X: 0.94 - 0.98 K; 1X: 1.0 - 1.1 K) which suggests the possibility that a second sublimation may be decomposing TMTSF and thereby introducing more impurities.

The length of the anodic oxidation was varied allowing for roughly 30% and 13% oxidation of the neutral TMTSF. The 30% oxidation required 3 to 4 days while the 13% oxidation was completed in about 40 hours. This short term oxidation was carried out so that earliest formed crystals could be used. The current density was kept low so that crystal growth was slow compared to diffusion.[3]

A major obstacle in determining the temperature dependent resistivity was the appearance of random "jumps"

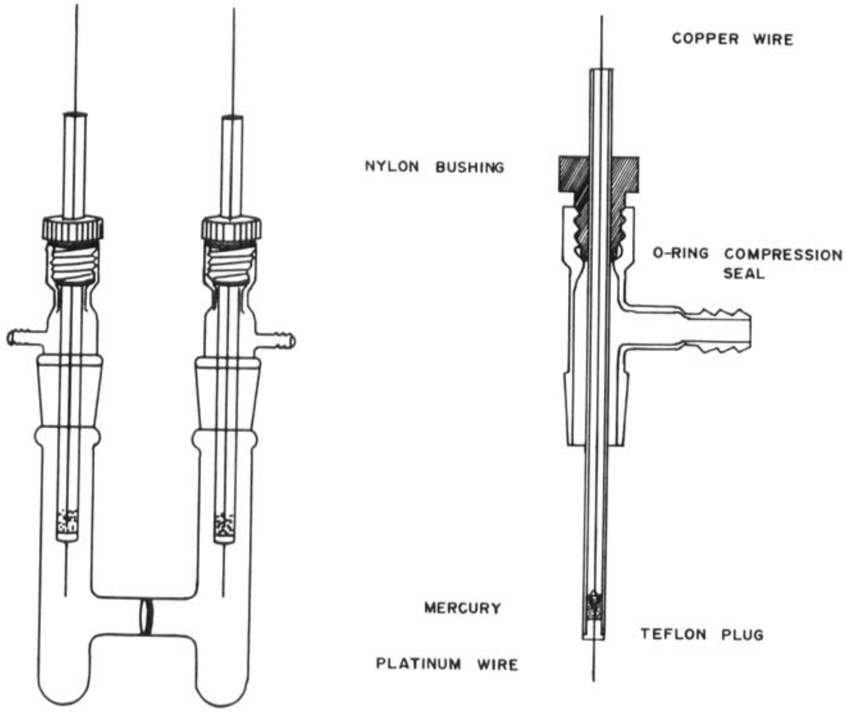


FIGURE 1 Electrochemical cell and inset

Table 1 Variation of Critical Temperature with Purity

Starting Purity	T_c of $(TMTSF)_2ClO_4$
Unsublimed TMTSF	0.8, 0.82
Once sublimed TMTSF	1.1, 1.0
Once sublimed TMTSF (short run)	0.98
Twice sublimed TMTSF	0.94, 0.98

in the data beginning slightly below 200 K in most samples. These "jumps" consisted of sharp irreversible increases in the measured resistance as the temperature was lowered. The problem was alleviated somewhat by mounting the sample in such a way as to introduce it to as little strain as possible. The "jumps" disappeared altogether in those samples grown by short term oxidation. This suggests that the "jumps" may be a result of thermal strain (which would be greater in this salt than in TTF-TCNQ due to the

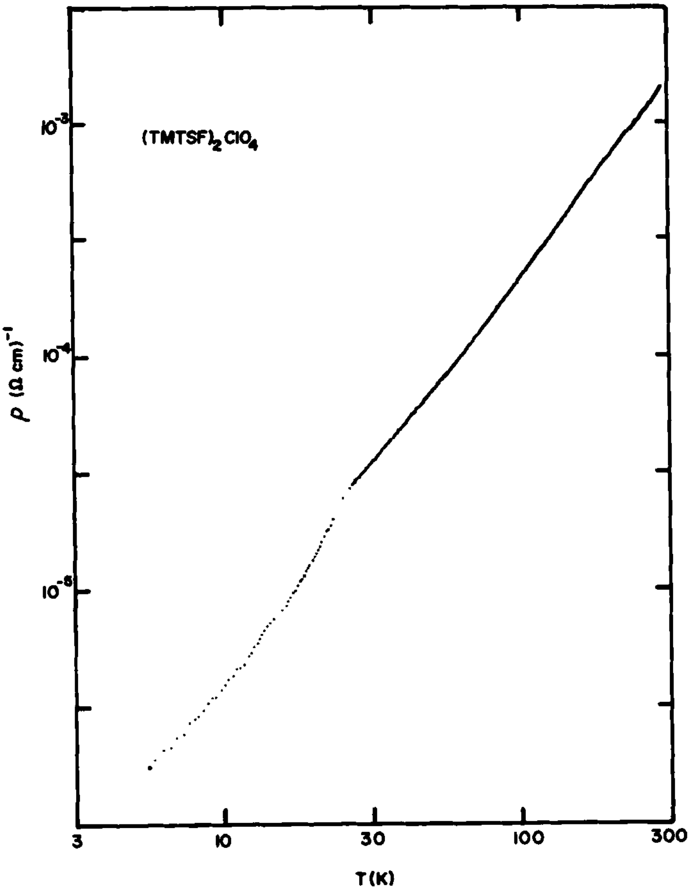
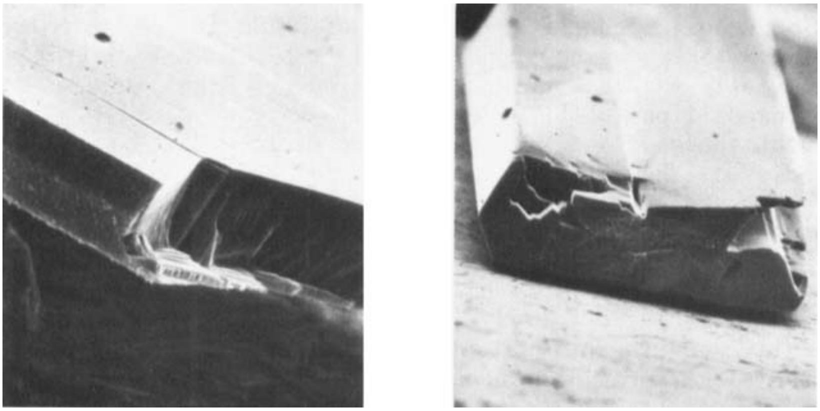


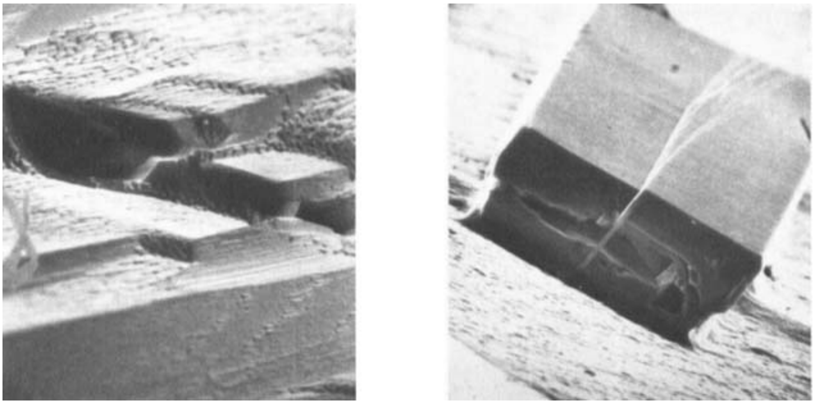
FIGURE 2 Resistivity of $(TMTSF)_2ClO_4$ from short term oxidation and once sublimed TMTSF

difference in the thermal parameters) and lattice defects inherent to the material. Figure 2 is a typical set of data from a crystal grown by short term oxidation. There



A fractured end of $(TMTSF)_2$-ClO_4 magnified 500 times

$(TMTSF)_2PF_6$ magnified 90 times



$(TMTSF)_2PF_6$ magnified 600 times

$(HMTSF)_3(PF_6)_2(C_6H_5Cl)_3$ magnified 230 times

FIGURE 3 Scanning electron micrographs (SEM's)

are no visible jumps as the conductivity increases from a value of 600 $(\Omega cm)^{-1}$ at 300 K to 6 x 10^5 $(\Omega cm)^{-1}$ at 4.2 K.

The external crystal morphology of $(TMTSF)_2ClO_4$ was examined by SEM (Figure 3). Unlike $(TMTSF)_2PF_6$, the micrographs reveal that $(TMTSF)_2ClO_4$ single crystals are more compact and exhibit a sheet-like appearance.

We have also begun preliminary work on salts of the HMTSF donor molecule. A solution of HMTSF in PhCl containing n-Bu_4NPF_6 as the supporting electrolyte was electrochemically oxidized using Pt electrodes. Single crystals of composition $(HMTSF)_3(PF_6)_2(PhCl)_3$ were obtained as black needles. A similar procedure yielded dark-brown needles of the AsF_6^- analog.

Crystallographic data for the PF_6 salt are as follows: monoclinic, space group C2/c, a = 30.35(2)A, b = 11.106(6)A, c = 19.875(7)A, β = 109.16(3)°, V = 6328A^3, Z = 4. Cell constants for the isomorphous AsF_6 salt are: a = 30.55(1)A, b = 11.139(5)A, c = 19.948(5)A, β = 109.26(3)°, V = 6409A^3. Density measurements via the neutral buoyancy method proved troublesome, possibly because of solvent exchange or surface effects. We have eliminated different crystal forms as an explanation by measuring the diffraction pattern, density and resistivity on fragments from the same crystal of the PF_6^- salt.

The structure of the PF_6^- salt has been determined by single crystal X-ray diffraction techniques (current R value of 0.14 with all atoms isotropically refined, based on 2482 data). The basic crystalline motif of $(HMTSF)_3$-$(PF_6)_2(PhCl)_3$ is depicted in the (001) projection of Figure 4. The salient feature of the crystal structure is the trimerized stacking of HMTSF molecules along the b axis. One HMTSF molecule is located at the origin and there are inversion-related molecules (through 0,1/2,0) centered at ca. (0.03, 0.35, 0.01) and (-0.03, 0.65, -0.01). The PF_6^- counterions and the PhCl solvent molecules lie between stacks of HMTSF molecules so that there are no close intercolumnar contacts. Interestingly, one of the PhCl molecules (located along a two-fold axis) is very tightly intercalated between adjacent HMTSF columns. Intermolecular Se···C distances range from 3.41A to 3.83A (van der Waals sum = 3.75A). These contacts are illustrated in Figure 5 along with the weaker Se···F(PF_6) contact at 3.35A (van der Waals sum = 3.35A). Thus, the structure of $(HMTSF)_3(PF_6)_2(PhCl)_3$ is dominated by weakly interacting columns of HMTSF donors, and we expect this system to behave more one-dimensionally than its distant relatives $(TMTSF)_2X$(X = PF_6^-, AsF_6^-, ClO_4^-).[2,4]

Also, we present in Figure 6 a comparison of the overall stacking patterns and individual overlap configurations for the donor stacks in the conducting form of TMTSF-TCNQ,[6] in $(TMTSF)_2AsF_6$,[4b] and in $(HMTSF)_3(PF_6)_2(PhCl)_3$. Surprisingly, the monomeric columns in TMTSF-TCNQ, the staggered dimeric columns in $(TMTSF)_2AsF_6$ (and its PF_6 and ClO_4

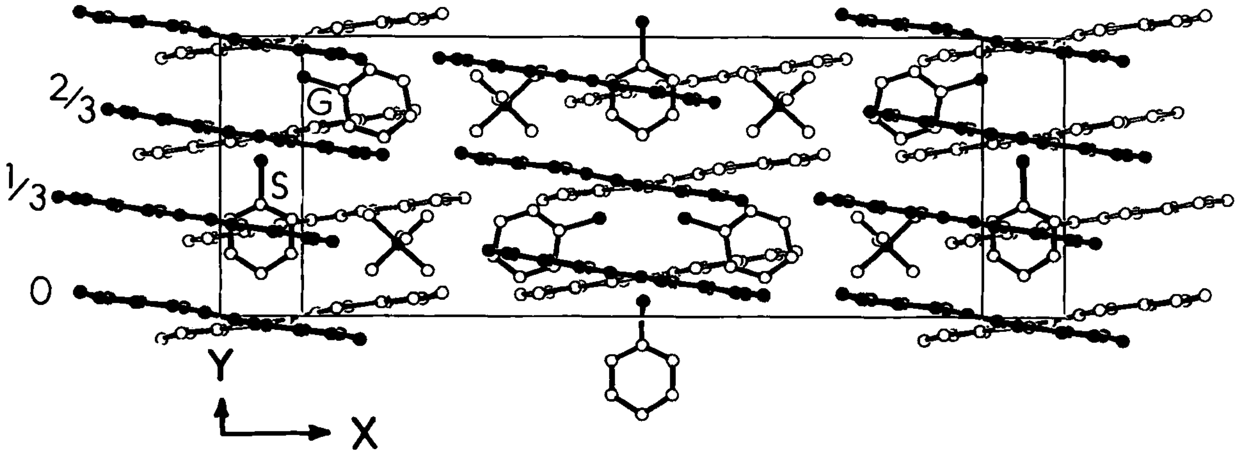


FIGURE 4 The (001) crystallographic projection for $(HMTSF)_3(PF_6)_2(PhCl)_3$, within the limits z = 0 to z = 1/2. Chlorobenzene molecules are differentiated by S (special position) and G (general position)

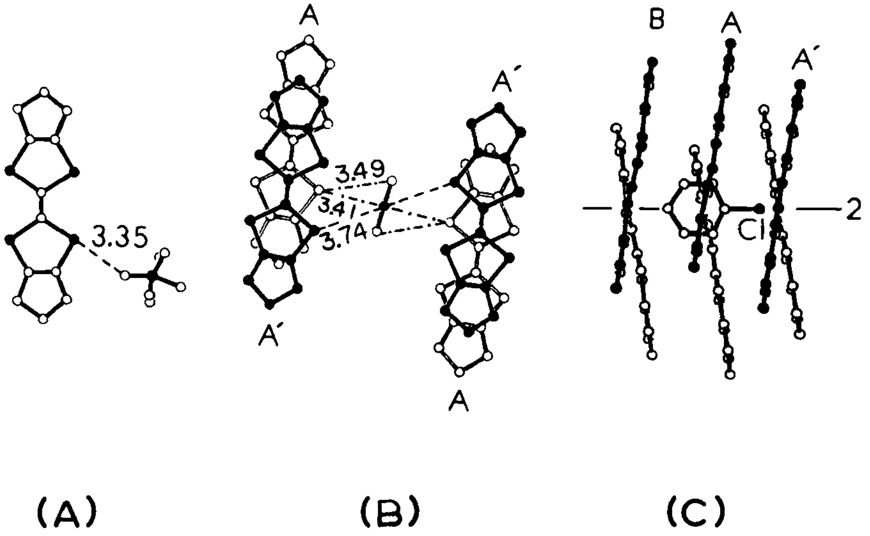


FIGURE 5 Illustrations for the principal intermolecular interactions in $(HMTSF)_3(PF_6)_2(PhCl)_3$

congeners[2,4]) and the staggered trimeric columns in $(HMTSF)_3(PF_6)_2(PhCl)_3$ all exhibit intermolecular overlap patterns and interplanar spacings which are virtually identical.

Trimerization of the HMTSF donor columns is consistent with a Peierls' instability[5] as the charge on the HMTSF molecule is fixed by stoichiometry (assuming full charge on the very electronegative PF_6 molecule) at +2/3 e, leading to a two-thirds filled donor band. However, the activation energy for this material is 2300 K, too large to result from a simple modulation of the bandwidth. Therefore, we suspect that the principal source of the insulating gap is the potential (with a period three times the basic donor spacing) due to the PF_6^- anions and the PhCl molecules.

In conclusion, the purity and crystal perfection of $(TMTSF)_2ClO_4$ can be increased by gradient sublimation of the TMTSF starting material and by short term electrochemical oxidation. The synthesis and study of HMTSF salts are underway and we report results for $(HMTSF)_2(PF_6)_2(PhCl)_3$.

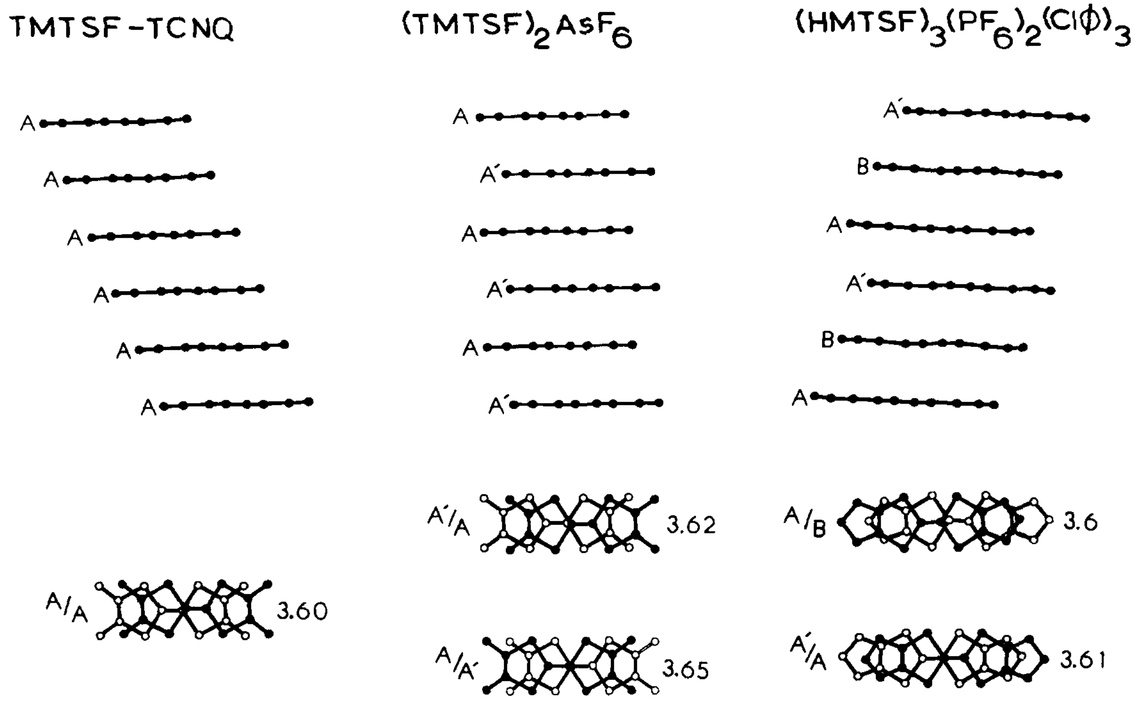


FIGURE 6 A comparison of the donor stacking and molecular overlaps in TMTSF-TCNQ, $(TMTSF)_2AsF_6$ and $(HMTSF)_3(PF_6)_2(PhCl)_3$

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