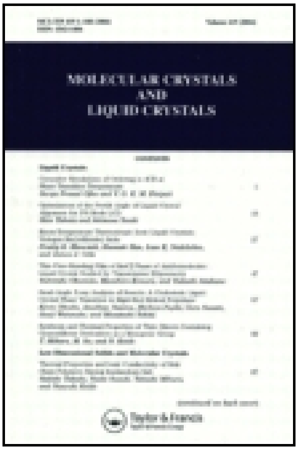

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$TMTSF_2X$ Salts. Preparation, Structure and Effect of the Anions

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$TMTSF_2X$ SALTS. PREPARATION, STRUCTURE AND EFFECT OF THE ANIONS.

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The preparation of the TMTSF molecule and some of its properties are reviewed. The preparation of metallic and superconducting $TMTSF_2X$ salts is described and some structural aspects are discussed, with emphasis of possible order-disorder transitions when X is a non-centrosymmetric anion. Preliminary results for $TMTSF_2TeF_5$ which remain conducting to at least 5 K are presented.

INTRODUCTION

Simple 2:1 salts of Tetramethyltetraselenafulvalene, TMTSF, exhibit a variety of physical properties. For example $TMTSF_2ClO_4$ is an ambient pressure superconductor below 1.4K whereas $TMTSF_2SiF_6$ is insulating at all measured temperatures. Naively all the solids in this isomorphous series of salts contain the same nearly uniform stack of TMTSF molecules where the electron energy band is created by carrier delocalization. The counter ions play no apparent role in the conduction process, but do influence the properties strongly by controlling the bandfilling and the subtle features of the lattice.

The most remarkable feature of the $TMTSF_2X$ salts is that the CDW instability observed in similar quasi one-dimensional organic conductors is extremely weak. Instead SDW instabilities and superconducting instabilities seem to dominate the low temperature properties unless the lattice is already distorted at higher temperature by interaction of the anions with the conducting stack.

TMTSF

TMTSF was first prepared in 1974[1,2]. In turn two TMTSF-TCNQ salts were identified[1]: one insulating(mixed stacks) and one metallic(segregated stacks. Later TMTSF-DMTCNQ was prepared[3] and it was shown that this materal under pressure remains metallic down to the lowest accesible temperatures[4], whereas at ambient pressure a Peierls transition at 41 K give rise to a semiconducting state[5]. It was shown that the charge transfer in TMTSF-DMTCNQ is ½ meaning that the CDW in this material is commensurate with the lattice[6]. Also it was shown that the donor stacks dominate the transport properties of the solid[5].

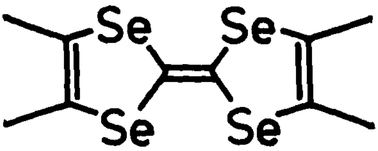
Based mainly on two features of this material: That commensurability does not lead to a substantial increase in the transition temperature and that the donor stack dominates the transport properties, it was decides to investigate single chain compounds of TMTSF, in the hope that they migth behave like TMTSF-DMTCNQ. Earlier it had been shown that in several selenium containing materials, it is possible to suppress the metal to insulator transition by hydrostatic pressure[7,8].

It was decided to use electrochemical oxidation of TMTSF in the presence of appropriate inorganic ions, based on the assumption that this technique would facilitate the formation of conducting phases since the crystal itself can act as the electrode (if conducting) whereas insulating phases would coat the electrode and stop the crystallization. The technique proved succesfull and has resulted in a large number of conducting TMTSF salts (and some insulating) most of which are of high purity and good crystallinity[9].

THE MOLECULE

TMTSF (Tetramethyltetraselenafulvalene,$\Delta^{2,2'}$-bi-4,5-Dimethyl-1,3-diselenolylidene) is isolated as dark violet needles decomposing above 250C. The material can be recrystallized from aromatic hydrocarbons, but is sparingly soluble in most common solvents at ambient temperature. Usefull solvents are chlorobenzene,dichloromethane,1,1,2-trichloroethane and THF where 10^{-2}-10^{-3} M solutions can be obtained.

TMTSF



TMTSF is conveniently purified by recrystallization from dry,deoxygenated toluene followed by gradient sublimation onto Teflon (165C, 10^{-5} torr). TMTSF is stable when stored under argon in the dark, but decomposes slowly, when exposed to the atmosphere.(A typical sign of decomposition is the smell of diacetyl).

The oxidation potentials of TMTSF are sligthly higher than those of the corresponding sulphur analogue (TMTTF), both in the gas phase and in solution. The photoelectron spectrum of TMTSF shows no dramatic differences when compared to the TMTTF spectrum.

It should however be noticed that the isotopic distribution of selenium as demonstrated by mass spectroscopy clearly show the "impurity" of natural TMTSF, a feature which influences the phonon,libration and vibrational spectra of TMTSF.

Recently a convenient approach to the synthesis of TMTSF has been published[10].

PREPARATION OF $TMTSF_2X$ SALTS

Single crystals of $TMTSF_2X$ are obtained by electrochemical[9] oxidation according to:

$$2\cdot n\ \mathrm{TMTSF} + n\cdot X^- \xrightarrow{-n\ e^-} (\mathrm{TMTSF}_2X)_n$$

A constant current technique has been used for the following reasons: Constant (low) current gives the possiblity of monitoring the crystallization rate throughout the experiment; and for experimental reasons (high internal cell-resistance, possible contamination from the reference electrode) it is more convenient.

In a typical experiment 10 ml of a 10^{-3} M TMTSF solution in CH_2Cl_2 containing n-butylammonium-X (0.1 M) is oxidized on a platinum rod (0.2 cm^2) with 5-10 µ amps to less than 60% conversion. The resulting crystals are harvested and washed with CH_2Cl_2 and dried. Elemental analysis are always in perfect agreement with 2:1 stoichiometry.

In table I are collected most of the $TMTSF_2X$ salts plus a few of different stoichiometry reported so far. The materials are grouped according to the symmetry of the anions. Also listed are transition temperatures for metal to insulator (M-I) transitions, their origin, and transition temperatures for superconductivity(T_{SC}) and critical pressures.

TABLE I. $TMTSF_2X$.

Anion	T_{M-I}K°	Origin	T_{SC}K°,	P Kbar	Ref
octahedral					
PF_6	12-17	SDW	0.9	6.5	9,11,12,13,14,15
AsF_6	12-16	SDW	1.1	12	9,16,17
SbF_6	17	-	0.4	11	9,18
TaF_6	-	-	1.4	12	18
NbF_6	12	-	absent,12		19
tetrahedral					
§ClO_4	absent	(SDW)	1.4 at 1 bar		20,21,18
ReO_4	180	diso.-o.	1.3	9.5	22,23,24
BF_4	40	-	-		9
BrO_4	"metallic"		-		25
IO_4	semicond.		-		26
planar					
NO_3	12	(SDW)	absent,12		9,27

§perdeutero-$TMTSF_2ClO_4$ behaves similarly[28]

Anion					Ref
non-symmetrical anions					
SO_3F	soft trans.		-		29
CF_3SO_3	soft trans.		-		19
TeF_5	cond. at 5 K		-		19

Other Stoichiometries

Br	(1:0.8)	semicond.	39
SCN	(1:0.5)	semicond.	39
Br_3	(1:0.8)	semicond.	19
NO_3	(1:1)	insul.	19
ΔR-SO_3	(1:1)	insul.	19
ΦSiF_6	(2:1)	insul.	19
TeF_5	(3:2)	semicond	19

ΔR = Phenyl or p-tolyl
Φdivalent anion

STRUCTURE

The basic feature of the structure of the isomorphous $TMTSF_2X$ salts is the zig-zag stack of the nearly planar TMTSF molecules parallel to a[30,20]. A side view is shown in fig. 1. The stacks are arranged in sheets with fairly close contact of Se atoms in neighbouring stacks. The close contact is not unique for $TMTSF_2X$ salts as TMTSF-DMTCNQ have similar contacts[3]. This interchain coupling is important in understanding the properties of $TMTSF_2X$ because it may result in strong curvature of the Fermi surface and coherent motion along b. This feature is still controversial and will not be treated here[32,33]. Table II gives the lattice parameters for several $TMTSF_2X$ salts.

From a crystallographic point of view strict uniformity of the stacks is not possible in the present structure type, and the sligth dimerization along a leads to a gap in the electronic band structure. This gap do however for monovalent anions not open at the Fermi level and does not in a first approximation influence the transport properties in the formally half-filled band material.

The anions exhibit a fairly close contact to the selenium atoms as seen in fig. 2 which show a view along a.

In the particular structure of the $TMTSF_2X$ salts the anions resides in an inversion center. Non-centrosymmetric anions (f.ex. ClO_4^- and NO_3^-) consequently occupy 2 equivalent positions statistically or are ordered and change the periodicity of the lattice. (Fig. 1 show the two positions of the ClO_4^- ion in $TMTSF_2ClO_4$). The ordering may have importent effects on the transport properties and actually various effect are seen depending on which particular anion is present. (See below)

PHYSICAL PROPERTIES

Details of the physical properties are treated in length elsewhere[32,33,34,35,36] and the intention here is just to classify some of the $TMTSF_2X$ materials after properties which seems to be directly related to the type of anion involved.

OCTAHEDRAL ANIONS (X = PF_6, AsF_6, SbF_6, TaF_6 and NbF_6).
All these salts exhibit high metallic conductivity to temperatures below 20 K. Then a M-I transition occur between 12 and 18 K. The M-I transition is the effect of a SDW distortion rather than the CDW distortion observed in similar materials. This was most clearly demonstrated by susceptibility measurements on oriented single crystals[15,17].

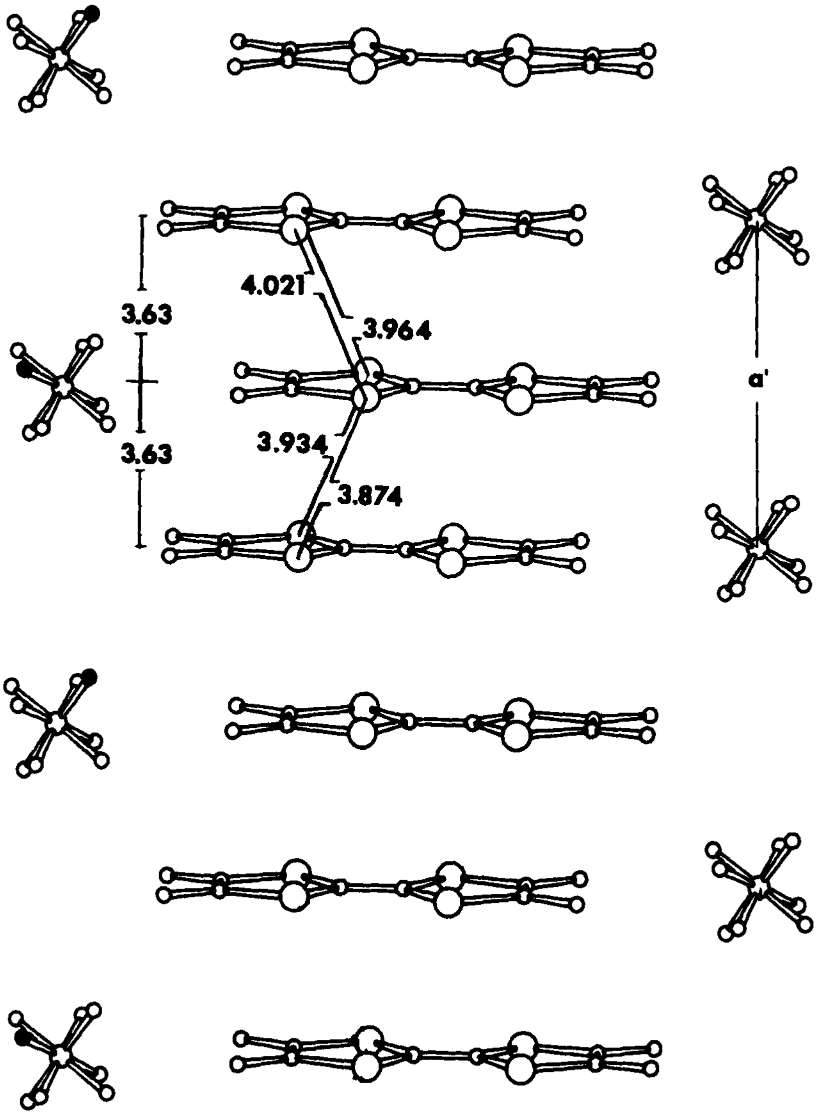


FIG. 1. Side-view of the stack in $TMTSF_2ClO_4$. The dimerization is clearly visible in the Se-Se intermolecular contacts. The left anion-column illustrates the potential 2 a ordering (as found for $TMTSF_2ReO_4$)

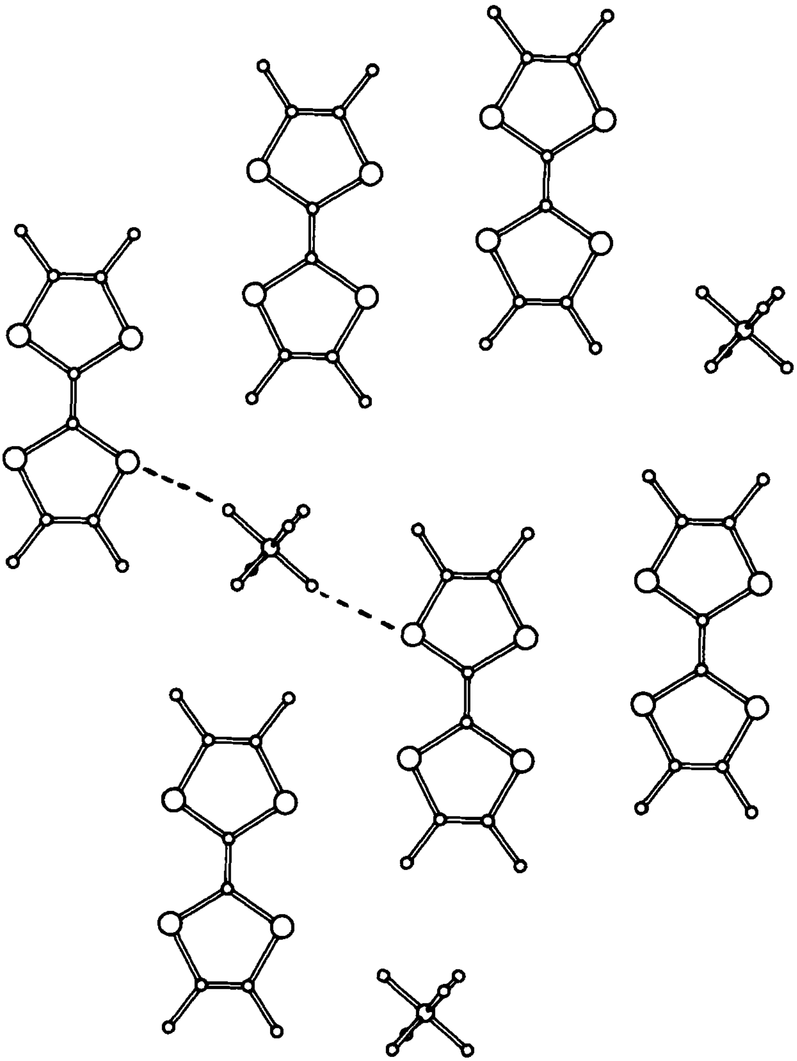


FIGURE 2. View along a for TMTSF$_2$PF$_6$.
The close anion- selenium contact is indicated by the dotted line.

TABLE 1. Unit cell dimensions (Å and deg) for various $TMTSF_2X$ salts.

Anion	PF_6	ClO_4	ReO_4
a	7.297	7.266	7.284
b	7.711	7.678	7.751
c	13.522	13.275	13.483
α	83.39	84.58	83.23
β	86.27	86.73	86.56
γ	71.01	70.43	70.08
V $Å^3$	714.3	694.4	710.5

Anion	SbF_6	TaF_6
a	7.299	7.280
b	7.728	7.716
c	13.901	13.918
α	82.77	82.88
β	85.23	85.37
γ	71.52	71.67
V $Å^3$	737.0	735.6

Data are collected at 300 K

All five salts are isostructural and crystallize in the triclinic space group $P\bar{1}$

In these salts hydrostatic pressure removes the SDW instability and instead metallic behaviour(above a specific critical pressure) is restored. Four of these materials in turn are superconducting around 1 K whereas a transition has not yet been observed in the less pure $TMTSF_2NbF_6$.

TETRAHEDRAL ANIONS (X = BF_4,ClO_4,ReO_4',BrO_4 and IO_4).
As shown in Fig. 1 the tetrahedral anion occupy two equivalent positions in P$\bar{1}$. At lower temperature the anions may order, but it is not a priori obvious how.

Examination of the naked anion lattice in the a-b plane[22] tend to favour periodicity a,b, xc and glide plane symmetry. It has also been argued that a smallalternating translation[23] will favour 2a,2b, xc.

The experimental results are diverging. There is thus so far no evidence for ordering in $TMTSF_2ClO_4$ which remain metallic down to 1.4 K where the material becomes superconducting.

In contrast $TMTSF_2ReO_4$ undergoes a M-I transition at 180 K[22]. This transition is observed simultaneously in conductivity, spin- and static susceptibility,thermopower and optical measurements and a gap of o.2 eV is estimated. Also structural evidence[24] show the development of a superstructure of 2a,2b,2c below 180 K. Thus the Fermi surface is completely destroyed at the transition. No 1-D precursor effects are observed. A detailed structural investigation below 180 K may resolvewhether the transition is driven by the coulombic interactions in the anion lattice or alternatively that the transition results from a "Peierls" instability where the main energy gain is associated with the quasi 1-D nature of the material.

At high pressure the metastable disordered state probably is stabilized to lower temperature and the superconducting state (at intermediate pressures in coexistence with the dielectric state) at 1.4K.[23]

The other salts of tetrahedral anions are less investigated . The BF_4 salts show a M-I transition below 41 K likely of the same origin as in $TMTSF_2ReO_4$. For the perbromate and the periodate the results are still unclear.

PLANAR ANION (X = NO_3)
$TMTSF_2NO_3$ is an interesting addendum to the perrhenate. At ambient pressure a metallic state persists[9] to 12 K where probably the SDW distortion sets in. The structural investigations[24] show a superstructure (2a,b,c) below 40 K. This transition is barely visible in the transport data at ambient pressure. Thus the anion ordering does not lead to

complete destruction of the Fermi surface.
Under pressure the M-I transition is suppressed but superconductivity has not been observed[27].

This may result from the fact that NO_3 is not as effective an electron acceptor as the other anions studied. Thus back transfer could occur under pressure and the resulting paramagnetic centers could act as pairbreakers.

DIPOLAR ANIONS (CF_3SO_3,FSO_3 and TeF_5)
These solids are less investigated. The FSO_3 ion appear[29] to be disordered at higher temperature. CF_3SO_3 has a narrow metallic regime at high temperature[19] but no sharp transition.

$TMTSF_2TeF_5$ show a soft resistance minimum around 70 K, but remains conducting to at least 5 K[19].

PURITY PROBLEMS/ALLOYING.
The $TMTSF_2X$ salts in most cases crystallize with very high purity in contrast to 1-D charge transfer salts in general, where magnetic impurities are generally a severe problem. The very high"accidental" purity of the $TMTSF_2X$ salts is a prerequisite for the observation of superconductivity in these salts . For example X-ray irradiation creating defects at the 100 ppm level wipe out the superconducting state[37] and likewise donor stack doping is extremely efficient[26,28]. It is also surprising that anion doping such as 7% ReO_4 in $TMTSF_2ClO_4$ suppressed a possible superconducting state to at least below 0.5K[38]. Note also that $TMTSF_2SbF_6$ is superconducting only below 0.4 K and that superconductivity is so far not observed in $TMTSF_2NbF_6$. Both these anions are hydrolytically unstable and small amounts of species such as SbF_5OH^- may be formed. Also i "pristine" $TMTSF_2ClO_4$ the T_{SC} depends on the crystal quality[38].
The twinning observed in most large crystals of these salts do not seem to effect the properties dramatically, although one migth expect the defect zones to contain trapped free spins.

OTHER STOICHIOMETRIES

Several other phases than the 2:1 has been observed. These materials have so far attracted less attention than the $TMTSF_2X$ salts. As Shown i Table I most of these materials are semiconducting or insulating. It should be mentioned that the first single chain salts of TMTSF prepared (Br and SCN) both exhibit the zig-zag structure[39]. The lattice is orthorhombic with long interchain contact and a disordered anion lattice.

The 1:1 salts seems to crystallize in alternating stacks with resulting insulating behaviour, whereas TMTSF$_3$TeF$_5$ crystallize in a triclinic cell with short interplanar contacts.

CONCLUSION

In conclusion the properties of TMTSF, and some properties of its salts with various inorganic anions have been reviewed. The role of the anions in the interplay with the conducting stack has been emphasized, and it has been argued that the"accidental" high purity of the materials is a prerequisite for the observation of superconductivity.

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