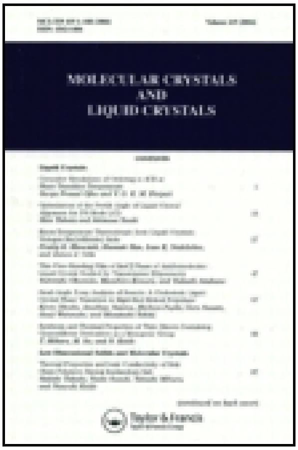

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On the Structure and Properties of TMTTF and TMTSF Salts: Experimental Evidence for the Importance of Interchain Couplings

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ON THE STRUCTURE AND PROPERTIES OF TMTTF AND TMTSF SALTS : EXPERIMENTAL EVIDENCE FOR THE IMPORTANCE OF INTERCHAIN COUPLINGS.

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The structure and physical properties of tetramethyltetrathiofulvalène (TMTTF) salts are reviewed. New results are given about $(TMTTF)_2\ PF_6$, $(TMTTF)_2\ C\ell O_4$ and the selenium analog $(TMTSF)_2\ C\ell O_4$. An experimental relationship is shown between the electrical and magnetic properties and the closest contacts S–S or Se–Se of neighbouring stacks.

I - INTRODUCTION

Few years ago we were investigating a new series of cation radical salts based on tetramethyltetrathiofulvalenium (TMTTF) (1).The electrical properties of these salts were not very high and they did not behave as truly metallic compounds. However they present some special features mainly a non-regular stacking of $TMTTF^+$ radical cations with an alternate overlapping.

The discovery of a metallic behaviour in Selenium analogs (2) (TMTSF) with a phase transition towards a superconducting state under pressure at low temperature (3) incited us to pursue this work. As sulfur and Selenium appeared to be isostoichiometric and isomorphous a comparative study should be done to understand the difference observed for the physical properties and to find the relevant experimental parameters connected with the occurence of a superconducting state.

In this paper we will briefly review the structure and the properties of TMTTF salts, giving new results specially on $TMTTF_2$-PF_6, $TMTTF_2$-$C\ell O_4$ and $TMTSF_2$-$C\ell O_4$. Finally we will show that a relationship exists between the described electrical and magnetic properties and the closest contacts S-S or Se-Se of neighbouring stacks.

II - CRYSTAL STRUCTURES OF TMTTF SALTS

The crystal structures are known for the salts with the following counterions : BF_4^-, SCN^-, Br^-, I^- (4), $C\ell O_4^-$ and NO_3^- (5). All compounds are triclinic (space group $P\bar{1}$) with parallel stacks of TMTTF molecules. The structure of $(TMTTF)_2\ PF_6$ is shown as the last known example in figures 1 and 2 with projection along b and a axis respectively.

A common feature of the series is the zig-zag configuration of the molecular stacks. This leaves cavities in which the counterions are located. Moreover the stacks are not regular, in the sense that there are two different distances (d_1 and d_2, fig.1) between consecutive molecules in the same stack : the TMTTF molecules form diads.

Figure 3 shows the molecular overlap of classical type for TTF family. It is seen that the TMTTF stacks form sheets parallel to (xOy) plane, with the counterions in between. The interaction between consecutive stacks in the sheets must be particularly effective through the nearest sulfur atoms. Each TMTTF molecule has two sulfur atoms which are in close contact with a sulfur atom of the neighbouring stacks. In Table 1 are given these S-S distances,which are different from one salt to another but always longer than the Van der Waals distance (3.70 Å) except for the bromine derivative. In table 1 are also

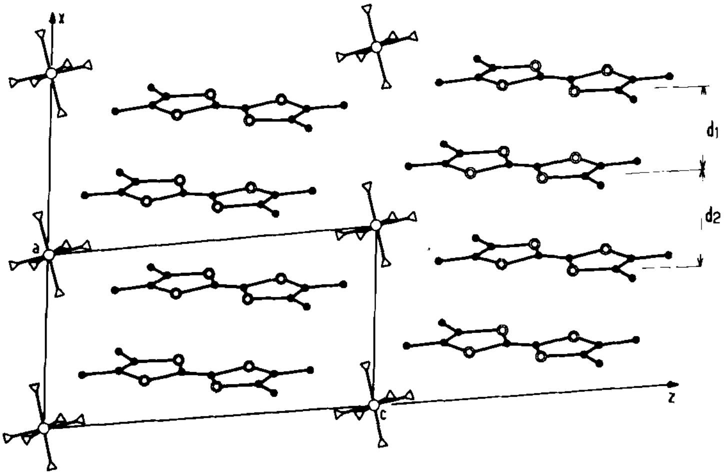

FIGURE 1 Crystal structure of $(TMTTF)_2PF_6$: projection along b-axis.

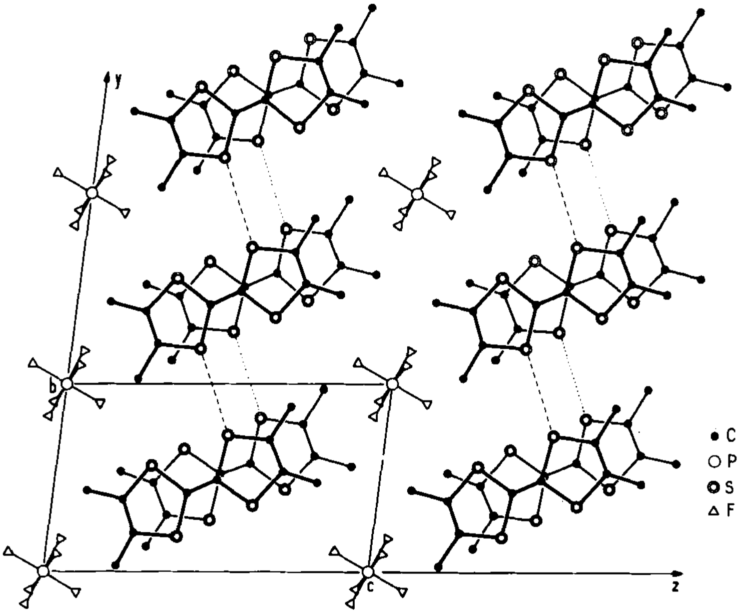

FIGURE 2 Crystal structure of $(TMTTF)_2PF_6$: projection along a-axis.

given the intrastack distances d_1 and d_2 : the diadic character, as measured by the difference $\delta = d_1 - d_2$ is more or less pronounced according to the counterion without any obvious rule.

Table 1 : Interstack and intrastack distances of TMTTF salts

	SCN^-	$C\ell O_4^-$	PF_6^-	BF_4^-	I^-	NO_3^-	Br^-
closest S-S interstack distance (Å)	4.01	3.99	3.99	3.88	3.80	3.79	3.73
Intrastack distances :							
d_1 (Å)	3.56	3.59	3.62	3.56	3.54	3.56	3.53
d_2 (Å)	3.49	3.52	3.52	3.54	3.50	3.50	3.50
$\delta = d_1 - d_2$ (Å)	0.07	0.07	0.10	0.02	0.04	0.06	0.03

III - PHYSICAL PROPERTIES OF TMTTF SALTS.

The electrical conductivity at room temperature is of the order of 40 to 100 $\Omega^{-1}cm^{-1}$, except for the bromine salt which presents the highest conductivity $\sigma_{RT} = 260\ \Omega^{-1}cm^{-1}$ (1). The temperature dependences generally exhibit a flat maximum and the compounds become insulating at low temperature. However, due to the brittleness of the crystals by cooling, the transport properties have to be studied very carefully; they will be presented elsewhere (6).

Static properties such as magnetic susceptibility are not sensitive to the brittleness. The paramagnetic susceptibility of $TMTTF_2$-PF_6 is shown in figure 3 as a function of temperature. As for every compound of the series the room temperature value is around $6\ 10^{-4}$ e m u/mole, a rather high value which could be due to electronic correlations (7). With decreasing temperature, the paramagnetism decreases slightly, then drops sharply and increases again at helium temperatures. The sudden drop indicates a phase transition. We have found the critical temperatures T_c = 15 K for $(TMTTF)_2\ PF_6$, 41 K for $(TMTTF_2)BF_4$ and 75 K for $TMTTF_2\ C\ell O_4$.

These phase transitions are responsible for an anomaly on the specific heat $C_p = f(T)$ curves (figure 4)

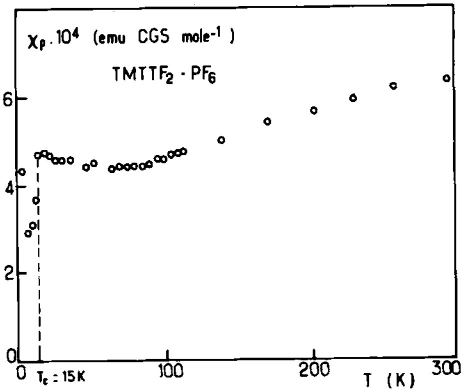

FIGURE 3 Paramagnetic susceptibility of $(TMTTF)_2$ PF_6.

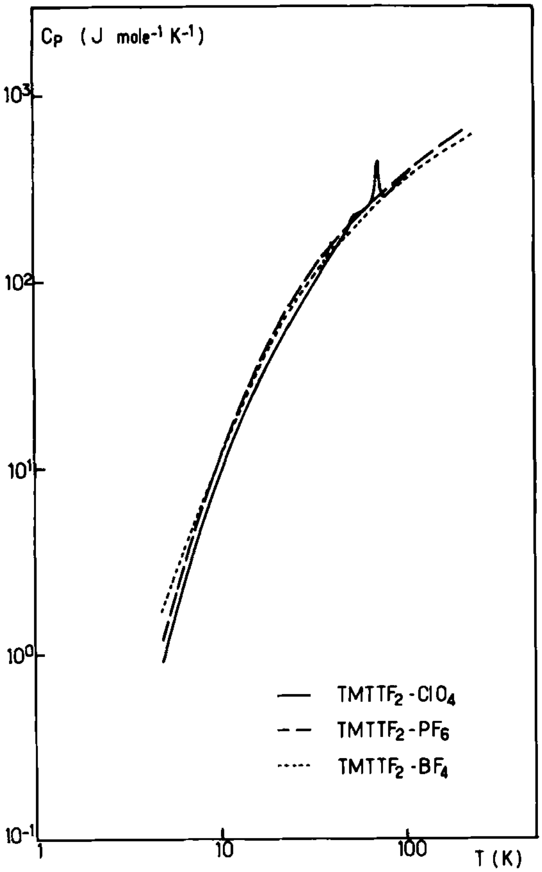

FIGURE 4 Specific heat C_p of TMTTF salts.

in the case of the BF_4 and $C\ell O_4$ salts but not for $(TMTTF)_2$ PF_6. The nature of the phase transition must be different for the PF_6 salt. It should be related to the symmetry of the anion : PF_6^- has a center of symmetry unlike BF_4^- and $C\ell O_4^-$ which are tetrahedral. From X-Ray diffuse scattering experiments, it has been shown that the metal-insulator transition in $C\ell O_4$ derivative is driven by the ordering of $C\ell O_4^-$ anions, whereas $(TMTTF)_2$ PF_6 exhibits a 1-D precursor scattering characteristic of a Peierls transition (8).

The phase transitions do not seem to affect the EPR linewidth and the g-factor value. In figure 5 are given the EPR results for PF_6 and $C\ell O_4$ salts, obtained with the static magnetic field parallel to the stacking axis. As usual for one chain compounds, the linewidth decreases almost linearly with decreasing temperature, whereas the g-factor is quasi independent on temperature. At about 20 K a maximum of linewidth appears on the curve corresponding to perchlorate compound. This anomaly could be due to the ordering of methyl groups.

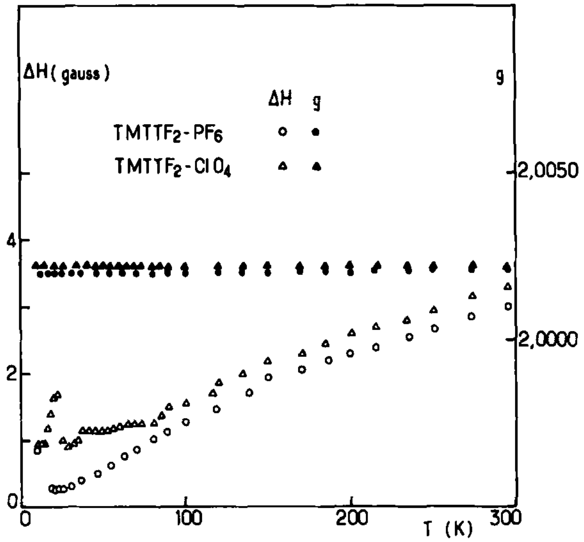

FIGURE 5 Linewidth and g-factor of TMTTF salts

The overall analysis of these results (6) shows that two kinds of situation occur :

- with the non-centrosymmetrical anions : an order-disorder transition of these anions exist at a higher temperature than the phase transition which could occur on the TMTTF stacks. It results an opening of the energy gap at the Fermi level.

- With the centrosymmetrical anions : The order-disorder transition does not exist and the "intrinsic" metal-insulator transition appears at a low enough temperature, below 20 K generally : $(TMTTF)_2$ Br is a typical case (T_c = 19 K).

IV - COMPARISON WITH TMTSF SALTS

The crystal structures of three TMTSF salts (with $C\ell O_4^-$, (9), PF_6^- (10) and AsF_6 (11) anions) are known at room temperature. These salts are isomorphous of TMTTF salts with a similar diadic character although less pronounced. The inter and intrastack distances are given in Table 2.

Table 2 Interstack and intrastack distances of TMTSF salts.

	$C\ell O_4^-$	PF_6^-	AsF_6^-
Closest Se-Se Interstack distance (Å)	3.77	3.88	3.90
intrastack distances :			
d_1 (Å)	3.63	3.66	3.65
d_2 (Å)	3.62	3.63	3.62
$\delta = d_1 - d_2$	0.01	0.03	0.03

The Se-Se distances are shorter than the Van der Waals distance (4.0 Å), in particular for the perchlorate salt, which displays a superconducting state at ambient pressure, the two others being superconducting under a pressure of several kilobars. The compactness along the stacking axis is also higher in TMTSF salts than in sulfur derivatives, as referred to the Se-Se or S-S Van der Waals distances respectively.

We have recently measured the temperature dependence of the g-factor and EPR linewidth of $(TMTSF)_2\ C\ell O_4$, from room temperature down to 4 K (12). The data are shown in figure 6. One component of the g-factor has a special behavior : constant down to 45 K, it increases regularly with a further temperature decrease. This increase might be related to the presence of 1 d superconducting fluctuations. The linewidth does not show any particularity : it decreases quasi linearly as for TMTTF salts with a change in the slope around 100 K.

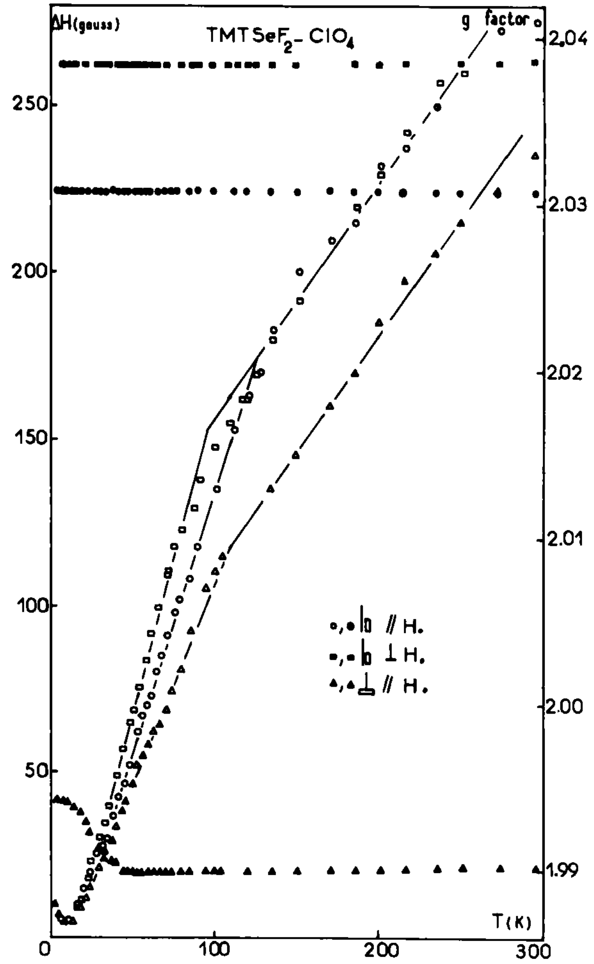

FIGURE 6 Linewidth and g-factor of $(TMTSF)_2\ C\ell O_4$.

Its value is much larger than for the sulfur analogs (compare figures 5 and 6) due mainly to the difference in spin-orbit couplings of sulfur and selenium atoms.

For the purpose of comparison the spin-lattice relaxation mechanism has to be involved. In these one-chain compounds which exhibit a temperature dependence similar with those observed in natural metals the principal relaxation mechanism is the modulation of the spin-orbit coupling by the phonons (12). In that case, where the ELLIOTT's relation is valid two independent parameters have to be considered (13) :

- The g-factor shift which depends also on the spin-orbit coupling.
- The dimensionality of the electronic system; in the case of a pure 1d electronic gas ang relaxation process is forbidden; when the electronic system is less and less 1 d the relaxation mechanism through the phonons is more and more efficient (7). Experimentally the observed linewidth is more and more broadened.

To take account of the first parameter it is necessary to normalize the experimental linewidth. In the case of atoms it is known that the mean value of the g-factor anisotropy $\overline{\Delta g^2} \sim Z^4$, where Z is the atomic number. In table 3 are given the anisotropies for the diagonal terms of the g-factor tensor in the case of the perchlorate and hexafluorophosphate salts. The calculated ratio of $\overline{\Delta g}^2$ for selenium and sulfur compounds is very close to the atomic ratio (Z_{Se}/Z_S) = 20.39. This result means that most of

Table 3 Anisotropy of g-values at room temperature.

Compounds	Δg_{xx}	Δg_{yy}	Δg_{zz}	$\overline{\Delta g}^2$	$\frac{\overline{\Delta g}^2_{Se}}{\overline{\Delta g}^2_S}$
$(TMTTF)_2PF_6$	-0.0003	0.0088	0.0067	0.408×10^{-4}	20.2
$(TMTSF)_2PF_6$	-0.0123	0.0377	0.0300	8.24×10^{-4}	
$(TMTTF)_2ClO_4$	-0.0001	0.0087	0.0067	0.402×10^{-4}	19.3
$(TMTSF)_2ClO_4$	-0.0123	0.0367	0.0287	7.74×10^{-4}	

the spin density lies on the S or Se atoms. It is possible therefore to use $\overline{\Delta g^2}$ as a measure of the spin-orbit coupling strength for these compounds; for a comparison between sulfur and selenium derivatives we will use the reduced linewidth $(S/\overline{\Delta g^2})$. In figure 7 these room temperature linewidths are plotted against the interstack S-S or Se-Se distances normalized with respect to the Van der Waals distances (see tables 1 and 2). A unique correlation is observed for both series of compounds which shows an increase of the linewidth with the interchain coupling. A similar relationship is observed for the room temperature conductivity (figure 7) : the absolute value at room temperature increases whereas the temperature of the conductivity maximum is going down. These experimental relationships show the importance of the transverse couplings along b-axis and the tendency toward a 2d electronic system.

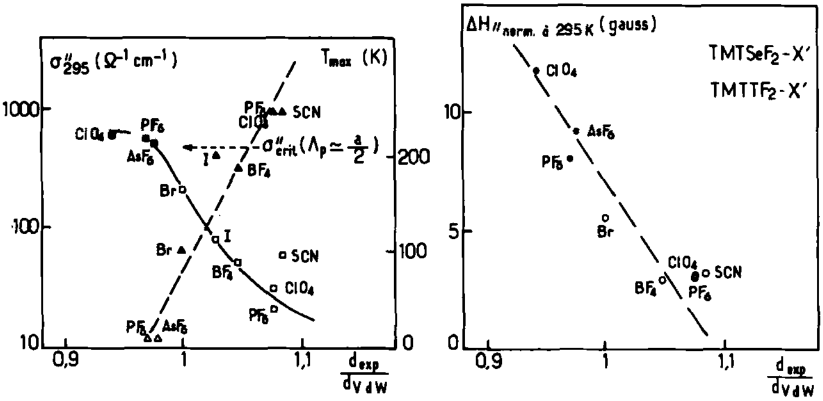

Figure 7 : Experimental relationships between the linewidth, the conductivity, the temperature of the maximum conductivity and the interstack S-S or Se-Se distances normalized to the Van der Waals distance.

V - CONCLUSION

This work clearly shows that the close contacts between sulfur or selenium atoms belonging to neighbouring stacks influence drastically the physical properties of the compounds in the series. It is striking to notice that the less one-dimensional compound $TMTSF_2 - C\ell O_4$ is also the only one which displays a superconducting state at ambient pressure. Furthermore, the bromine derivative of TMTTF which becomes superconducting around 4 K under 25 kbar (14) is also the less one dimensional compound in the TMTTF series.

A second crucial parameter is the nature of the counterion. The instabilities which occur in these compounds depend on the symmetry and on the size of the counterion (6). This analysis might help to orientate the synthesis of new superconducting organic materials.

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