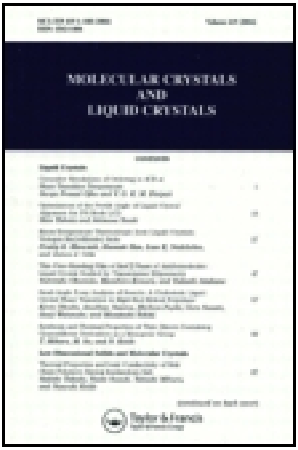

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PHYSICAL AND STRUCTURAL PROPERTIES OF A NEW SERIES OF RADICAL-CATION SALTS BASED ON THE TETRASELENAFULVALENE BACKBONE : $DMtTSeF_2 - X$

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Abstract We have synthetized and purified the dimethyltrimethylene tetraselenafulvalene (DMtTSeF). From this unsymmetrical molecule a series of radical cation salts has been prepared by electro-oxidation. This new series, isostoicheiometric and isomorphous with the TMTSeF salts, exhibits a metallic behavior down to 0,1 K without any sign of either a metal-insulator or a superconducting phase transition.

The synthesis of new compounds with the tetraselenafulvalene (TSeF) backbone but with different substituents on the fulvalene rings is a way to search for an antiferro (AF) or superconducting (SC) state at low temperature. The dimethyltrimethylene tetraselenafulvalene (DMtTSeF) which presents two methyl groups on one side and a planar cycle on the other side is a favourable unsymmetrically alkylated precursor molecule (1). Its salts can give a molecular stacking with both cages for the anions and enhanced crystal packing with stronger electronic transverse interactions.

This point is supported by the structural evidences which show that in TMTTF/TMTSeF salts the organic molecules are not anymore centro-symmetric because of the low symmetry of the surroundings (2). Besides, the knowledge gained on C.T.C. (3) as well as on the sulfur analog salts (4) have demonstrated that a regular stacking of unsymmetrical molecules occurs without any signifiant disorder.

Chemical preparation :

As already described (1) the selone coupling gives rise to a mixture of the three expected molecules. The residue is recrystallized from cyclohexane which is further purified by chromatography on a Kieselgel Column : then the DMtTSeF molecule is almost completely separated. In a first synthesis a very small amount of TMTSeF (up to 1 %) has been detected. Then a second preparation has been done in which about 2 % of unknown impurities have been detected. By gas chromatography on a capillary column coupled with mass spectrometry we have found that the main impurity is the analog of the DMtTSeF molecule where one Se has been changed by a S atom on the dimethyl selone.

Several radical cation salts have been prepared by the classical technics of electro-cristallization. Small and black single crystals are grown as presented in table 1.

Excepted for the nitrate salt the other salts of stoicheiometry 2-1 are highly conductive at room temperature.

Salts	$\sigma_{\parallel}$ Ω^{-1} cm^{-1} at 295K
1st batch :	
$(DMtTSeF)_2$- ClO_4	1000 - 1300
$(DMtTSeF)_2$- AsF_6	1200 - 1500
$(DMtTSeF)_2$- PF_6	500 - 600
2nd batch :	
$(DMtTSeF)_2$- ClO_4	~ 500
$(DMtTSeF)_2$- ReO_4	300 - 700
$(DMtTSeF)_2$- SbF_6	300 - 500
$(DMtTSeF)_x$ - NO_3	insulator

Table 1 ROOM TEMPERATURE CONDUCTIVITY MEASURED ALONG THE NEEDLE AXIS

X-ray structure :

The crystal structures have been carried out at room temperature on two salts ; perchlorate and hexafluoroarsenate. It appears that these salts are isomorphous with the TMTSeF salts : they cristallize in a triclinic system, space group P $\bar{1}$, with very similar unit cell parameters (5) (6). One projection of the DMtTSeF$_2$ - ClO$_4$ crystal structure is presented in figure 1.

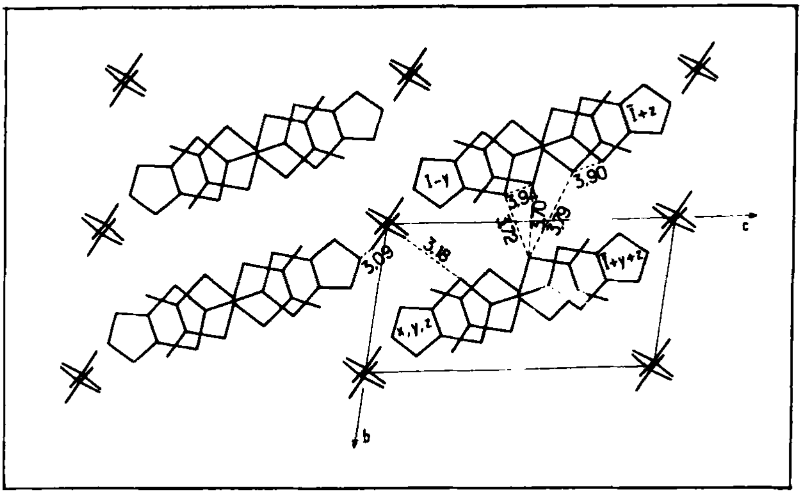


Figure 1 : **Room temperature crystal structure of DMtTSeF$_2$- ClO$_4$: projection in the plane (b,c). (Unit cell parameters : a = 7,340 Å, b = 7,696 Å, c = 13,414 Å, α = 99°,49, β = 87°,63, γ = 110°89 and V = 698.17 Å^3)**

Several features are noteworthy : - an ordered array of the organic molecules which form centrosymmetric dimers with the zig-zag stacking mode and cages for the counter-ion - Two equivalent sites for the ClO$_4^-$ anion with a distance between the Cl positions of 0.44 Å along the b axis ; this dynamical disorder should give rise to some ordering process at a lower temperature.

The main characteristic distances are reported on table 2 together with those of the similar TMTSeF salts. Two essential differences are detected, on one hand the (Se...Se) shortest interstack

Distances (Å) / Compounds		Intrastack characteristics		Interstack coupling	Anion-cation interaction
			shortest	shortest	
	d_1	, d_2	$(Se...Se)_{intra}$	$(Se...Se)_{inter}$	(Se...O or F)
$(TMTSeF)_2$- ClO_4 (5) (6)	3.63	3.64	3.73	3.78	3.32
AsF_6	3.62	3.65	3.77	3.91	3.27
$(DMtTSeF)_2$ ClO_4	3.66	3.68	3.90	3.70	3.18
AsF_6	3.66	3.67	3.91	3.72	3.26

Table 2 ROOM TEMPERATURE CHARACTERISTIC DISTANCES : A COMPARISON BETWEEN TMTSeF AND DMtTSeF SALTS

distances and on the other the anion-cation distances, which are smaller than in the TMTSeF salts.

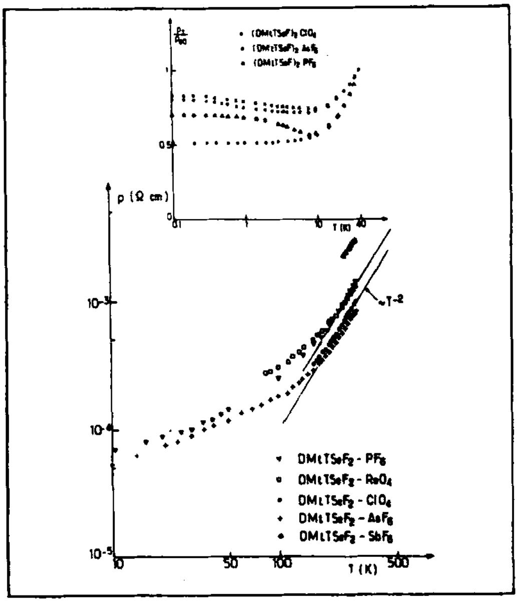


Figure 2 : Log-Log plot of the d.c electrical resistivity versus temperature measured along the needle axis for the given DMtTSeF salts. In insert the very low-T behavior is given for the salts issued from the first batch (see table 1).

Physical properties :

The d.c electrical resistivity temperature dependences have been done on every salt. Because of the brittleness of these crystals in several case we have not be able to accomplish a complete run. As presented on figure 2 we recognize two regimes :

- At high temperature (T > 200 K) a metallic behavior with $\rho \propto T^{-2}$ as in TMTSeF salts (7) ; below 200 K a regime change occurs characterized by the flattening of the experimental curves.

- At low temperature (0,1 K < T < 40 K) the resistivity saturates for all the compounds and becomes almost constant below 4 K with some change from one crystal to one another belonging to the same batch (see insert of figure 2).

The thermoelectric power has been measured for the AsF_6 salt (figure 3). The observed temperature dependence confirms the metallic regime with a small positive value falling linearly with temperature down to 60 K. Below this temperature the T.E.P. curve flattens out at the opposite of the $TMTSeF_2$ - AsF_6 salt on which a phase transition is detected around 15 K (7).

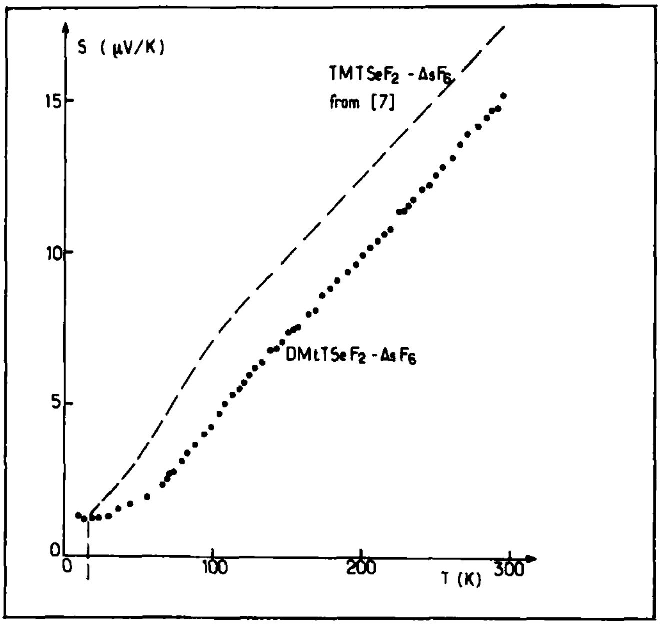
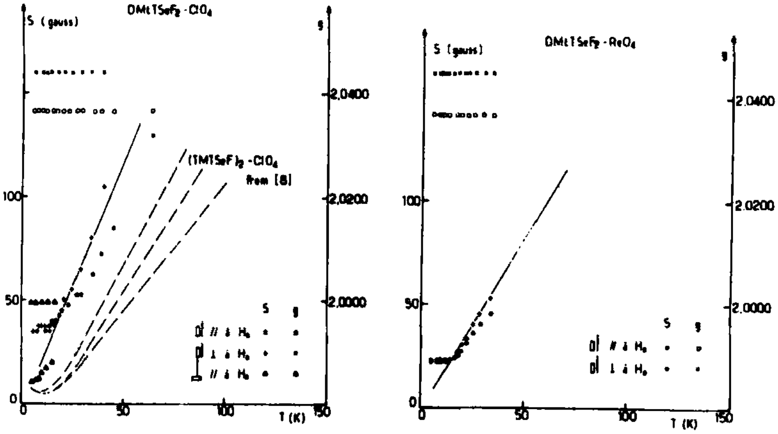


Figure 3 : Thermopower versus temperature for $DMtTSeF_2$- AsF_6 salt ; the dotted line shows the similar T. dependence already obtained on the corresponding TMTSeF salt.

Assuming a 1-d tight binding model for free electron gas and neglecting the weak dimerisation of the organic stack it is easy to estimate the longitudinal overlap integral $t_{\parallel} \simeq 0.30$ ev. This value corresponds to an estimate bandwidth of about 1.2 ev as in TMTSeF salts.

The E.S.R. experiments have been done at low T only with a standard X-band spectrometer. Indeed on single crystals no signal is detected at room temperature but only below 50 K. For two different salts the linewidth and g-factor principal components are presented in figure 4. Concerning the perchlorate salts we have also plotted our previous results on linewidth obtained for $TMTSeF_2 - ClO_4$ single crystals (8). Although the g-factor values are very similar we observe a larger linewidth for this new compound. A similar conclusion is reached with the perrhenate salt even if in both cases a low temperature plateau is observed. We can afford therefore that this linewidth increase at low temperature should be due to the presence of a more 2d electronic system compared to the TMTSeF series. This result agrees with the X-ray



Figures 4 : E.S.R. Linewidth and g-factor temperature dependences for the perchlorate and perrhenate salts.

determinations which exhibit enhanced interstack interactions (see table 2).

Concluding remarks :

We have shown that organic metals can be prepared from unsymmetrical precursor molecules. They form regular stacks of centrosymmetric dimers in rather strong interaction with the involved anions.

Nevertheless it turns out that we observe some impurity effect at low temperature on transport properties (d.c electrical resistivity and T.E.P.) as well as on ESR linewidth. A constant term is always present in the helium temperature range which appears to preclude any intrinsic behavior.

Some basic questions are not solved yet :

i) About the role of the anions ; we don't detect any experimental evidence of an ordering phase transition for non-centrosymmetric anions (ClO_4^- , ReO_4^-).

ii) No sign of either an antiferromagnetic or a superconducting phase transition at low temperature. These ground states are not observed because of the presence of impurities (∿ 1-2 % acting as a doping agent).

However, if it is well known that the SC phase is very sensitive to any perturbation or defect, the situation is not so drastic for the AF state. This is evidenced by the investigations on TMTSeF$_2$ - PF$_6$ doped with tetramethyldithiadiselenafulvalene (9) and on TMTSeF$_2$ - ClO$_4$ alloyed with TMTTF (10).

We can conclude therefore that the nature of the ground state in this new series of radical cation salts has to be elucidated yet.

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